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THE ORIGIN OF SEDIMENTARY IRON FORMATIONS: THE BIWABIK FORMATION OF THE MESABI RANGE.

JOHN W. GRUNER.

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INTRODUCTION.

Few problems of geology have offered such difficulties as the explanation of the origin of the large sedimentary iron ore deposits—for example, those of the Lake Superior region, especially the Mesabi Range. The source of the iron is as yet uncertain, as are the means by which the iron is dissolved and transported. The most probable hypothesis is that the iron of the iron-bearing formations, such as the Biwabik, may be derived from igneous and sedimentary rocks by ordinary processes of weathering, carried to the sea by rivers rich in organic matter, and deposited by microörganisms.

The writer is indebted to Dr. W. H. Emmons and to Dr. F. F. Grout for many valuable suggestions and criticisms during the progress of the work. Thanks are also due to the officials of many of the operating companies of the Mesabi range, especially to Mr. J. Uno Sebinius, general mining engineer, and to Mr. J. F. Wolff, geologist, of the Oliver Iron Mining Co.

GENERAL GEOLOGY.

Stratigraphy.

In the following description only the central and western part of the Mesabi Range will be treated,[1] but with few minor modi-

[1] For detailed descriptions see:

Winchell, N. H., and Winchell, H. V., "Iron Ores of Minnesota," Geol. Nat. Hist. Surv. Minn. Bull. 6, 1891.

Winchell, N. H., "Some Problems of the Mesabi Iron Ore," Geol. Nat. Hist. Surv. Minn., 21st Ann. Rpt., 1893, p. 134.

Winchell, H. V., "The Mesabi Iron Range," Geol. Nat. History Surv. Minnesota, 20th Ann. Rept., 1891.

Spurr, J. E., "The Iron-bearing Rocks of the Mesabi Range," Geol. and Nat. Hist. Survey of Minn., Bull. 10, 1894.

fications, most of the statements may be applied to the Eastern Mesabi and Gunflint ranges. The total length of these ranges from a point west of Pokegama Lake to the west end of North Lake, Canada, is about 175 miles.[2] The widths of the ranges vary considerably. The Biwabik formation has been found at a depth of 2,200 to 2,700 feet, 5 miles south of the town of Biwabik. The stratigraphic succession of the Huronian rocks in the Mesabi district is as follows:

Upper Huronian	Virginia slate Biwabik formation (iron-bearing) Pokegama quartzite.
Unconformity	
Lower-Middle Huronian	Giants Range granite Slate-graywacke-conglomerate formation.

The Upper Huronian rocks lie on the truncated older sediments and intrusives.

Biwabik Formation.—The Biwabik formation rests on the Pokegama quartzite practically conformably. A thin conglomerate is at its base. This conglomerate represents hardly more than a very short, if any, erosion interval. A vertical section of the subdivisions of the Biwabik formation is given below. The four larger divisions are essentially those of Wolff's[3] classification.

Upper Slaty Division.

Limy carbonate, with greenalite, greenalite slate, and slaty taconite .	0 to 25
Slaty, and cherty taconite, greenalite and slate	0 to 145

Upper Cherty Division.

Cherty, banded, slaty, and greenalite taconite with layers of conglomerate and algal structures. Some beds rich in magnetite	95 to 250

Leith, C. K., "The Mesabi Iron-bearing District of Minnesota," U. S. Geol. Survey, Mon. 43, 1903.

Van Hise, C. R., and Leith, C. K., "The Geology of the Lake Superior Region," U. S. Geol. Survey, Mon. 52, 1911.

[2] If the Animikie district of Ontario is included, this belt is 300 miles long.

[3] Wolff, J. F., "Recent Geologic Developments on the Mesabi Iron Range, Minnesota," *Proc. Lake Sup. Min. Inst.*, 1917, p. 229.

Lower Slaty Division.

Slaty taconite, greenalite, greenalite slate, banded and cherty taconite, carbonates and scattered conglomerates. Some rich magnetite beds	0 to 250
"Intermediate Slate." Black slate, greenalite slate and paint rock	½ to 40

Lower Cherty Division.

Lean member. White cherty and greenalite taconite, greenalite and greenalite slate	12 to 52
Member rich in magnetite. Irregularly banded, mottled and greenalite taconite	90 to 250
Member with iron in ferric state.	
Beds of cherty and banded taconite with slate and slaty taconite on top	8 to 70
Red basal taconite	0 to 40
Basal conglomerate and algal structures	0 to 12
Total	400 to 755

Detailed explanations of the terms used in this table have been given by Grout and Broderick.[4] Taconite is a word locally applied to almost any phase of rock of the iron-bearing formation. It includes ferruginous, sideritic, calcareous, and amphibolitic cherts, and greenalite rock, all ranging from granular to slaty phases.

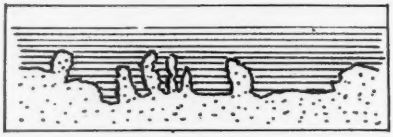


FIG. 42. Stylolitic surface between carbonate and slate in the Biwabik formation. Natural size.

A few new observations are here recorded. Amphiboles which were formerly thought to occur only east of Mountain Iron have been found throughout the whole range in considerable amounts. Siderite, as well as mixed carbonates, occurs abundantly in places. Considerable graphite has been observed by the writer in the cherts.[5] It occurs in very irregular black films. In cross sec-

[4] Grout, F. F., and Broderick, T. M., "The Magnetite Deposits of the Eastern Mesabi Range, Minnesota," Minn. Geol. Survey, Bull. 17, 1919, p. 14.

[5] Steiger reports organic matter from greenalite. Van Hise and Leith, *op. cit.*, p. 167.

tion these layers are typical styolites.[6] (See Fig. 42.) They are more abundant in the carbonates of the ferruginous cherts than where carbonates are absent. Recent study[7] has shown that magnetite is the most abundant iron oxide of the unweathered iron-bearing formation. In amounts sufficiently large to attract an ordinary horseshoe magnet, it is observed as aggregates of the size and shape of greenalite granules, and in dense fine-grained bands between cherty or slaty material. These bands may be straight, or irregular and contorted. Rarely they are two inches wide (on the East Mesabi, as much as 6 inches). Their usual thickness is from about ½ to ¾ inch. They consist largely of magnetite with a little siderite. Such bands of magnetite are commonly not directly in contact with chert. Very thin bands of carbonates separate the chert from the magnetite. In many places magnetite seems to have replaced carbonate, and it appears to be least abundant where much siderite is present. This suggests that in places, magnetite is formed by partial oxidation of siderite.

Structures whose significance had escaped notice until recently are the so-called algal structures, of organic origin,[8] which were described by Grout and Broderick on the East Mesabi and Gunflint ranges, and which have been traced westward by the writer. The structures look like fine, closely spaced, contorted lines resembling the grain of an especially gnarled and knotty piece of wood. The algal layers usually do not exceed a few feet in thickness, and in some places are only a few inches wide. One of the layers which has been traced throughout the Gunflint and

[6] Gordon, C. H., "On the Nature and Origin of the Stylolitic Structure in Tennessee Marble," *Jour. Geol.*, vol. 26, 1918, pp. 561–567.

[7] Wolff, J. F., *op. cit.*

Grout and Broderick, *op. cit.*

Broderick, T. M., "Economic Geology and Stratigraphy of the Gunflint Iron District, Minnesota," ECON. GEOL., vol. 15, 1920, p. 422.

Gruner, J. W., "Paragenesis of the Martite Ore Bodies and Magnetites of the Mesabi Range, Minnesota," ECON. GEOL., vol. 17, 1922, pp. 1–14.

[8] Grout and Broderick, "Organic Structures in the Biwabik Iron-bearing Formation of the Huronian in Minnesota," *Am. Jour. Sci.*, vol. 48, 1919, p. 199.

Broderick, T. M., "Detail Stratigraphy of the Biwabik Iron-bearing Formation, East Mesabi District, Minnesota," ECON. GEOL., vol. 14, 1919, p. 441.

Mesabi ranges is at the bottom of the Biwabik formation, closely associated with the basal conglomerates. Another is in the Upper Cherty division. It was not observed farther west

FIG. 43. Tracing of an organic structure from the algal structures of the Upper Cherty in the Gunflint formation. ×80. Slide M. 561. A portion of this organism is shown in Plate VII., *B*.

than the Hull-Rust mine at Hibbing, but to the east this algal formation is of the same persistence as the basal bed. It is also associated with conglomerates. These conglomerates are as persistent as the algal structures. They have been described in detail by Grout and Broderick.[9]

One excellent horizon-marker is the so-called Intermediate Slate, which on weathering forms the well-known "Intermediate Paint Rock" of the mines. Similar slaty layers can be traced for many miles, though they may not be thicker than a foot or two in places.

Original Extent of the Biwabik Formation.

The area of the Biwabik formation not covered by the slate has been estimated as 135 square miles;[10] that of the Gunflint formation does not exceed 10 square miles. Assuming much erosion and the gradual thinning out of the formations, the total area originally covered by the Biwabik and Gunflint formations may be estimated as 5,000 to 10,000 square miles. The writer examined the cores of over a thousand drill holes in the solid un-

[9] *Op. cit.*, p. 20.

Also: Grout, F. F., "The Nature and Origin of the Biwabik Iron-bearing Formation of the Mesabi Range, Minnesota," ECON. GEOL., vol. 14, 1919, p. 458.

[10] Van Hise and Leith, *op. cit.*, p. 164.

weathered formation alone, and the greatest thickness of the Biwabik formation found was 750 to 760 feet. At the west end of the range the formation thins out to less than 400 feet. Still more thinning occurs on the east end,[11] and an average thickness of 330 feet has been given by Broderick[12] for the Gunflint formation. Probably 550 feet would represent the average thickness of the exposed Biwabik formation. For a sheetlike sediment with an area of 5,000 to 10,000 square miles, an average thickness of 330 feet may be a fair estimate. The explored portion of the iron-bearing formation contains an average of a little more than 25 per cent. iron and has a specific gravity of 3.0 to 3.1. Thus, the total amount of iron in 10,000 square miles of formation 330 feet thick would be about 1,940,000 million metric tons.

Formation of Oölites and Similar Granules.

Link's[13] experimental work has shown that calcium carbonate, when precipitated as finest mud, will form oölites. Essentially the same thing is reported by Vaughan.[14] Brown[15] comes to the conclusion that oölites are produced either by algæ or similar organisms, or chemically by precipitation. The tendency now is to favor more the organic origin of deposits in cases in which it may be either inorganic or organic, since bacterial and other microörganic action are now being recognized.[16] It is also possible that inorganic and organic formation of oölites can go on side by side, or that organisms cause precipitation of colloids, while the actual shaping of oölites is due to the "tendency of the

[11] Grout and Broderick, *op. cit.*, p. 24.

[12] *Op. cit.*

[13] Link, G., "Die Bildung der Oolithe und Rogensteine," Neues Jahrb., Beilage Bd. 16, 1903, pp. 495–513.

[14] Vaughan, T. W., "Remarks on the Geology of the Bahama Islands and on the Formation of the Floridian and Bahaman Oölites," *Jour. Wash. Acad. Sci.*, vol. 3, 1914, pp. 302–304.

[15] Brown, T. C., "Origin of Oölites and the Oölitic Texture in Rocks," *Bull. Geol. Soc. Am.*, vol. 25, 1914, p. 772.

[16] See, for example: Drew, G. H., Papers from the Tortugas Laboratory, Carnegie Institution, Washington, vol. 5, 1914, p. 44.

Wethered, E. B., "The Formation of Oölite," *Quart. Jour. Geol. Soc.*, vol. 51, 1895, p. 205.

droplets forming during the separation of the dispersed phase of an emulsoid to coalesce," as expressed by Bucher.[17]

The cause of the formation of concentric layers in oölites has been studied by Schade,[18] who comes to the conclusion that in a deposit consisting mostly of colloidal material (gel), the tendency for the formation of concentric rings is less than in a mixture of crystalloids and colloids. Bucher[19] thinks that the rate of formation of the spherulites is important, those forming rapidly being more or less without definite structure. He also says that "the amount of other substance thrown out simultaneously with, and mechanically enmeshed in, the growing structure" has some effect on the structure. In the Biwabik formation are three kinds of granules:

1. Typical oölites made up of concentric layers. They consist of red jaspery or black graphitic (?) material with a center of the same material or of fine-grained chert. Spurr[20] and Leith[21] have called attention to them. They do not make up one per cent. of all the granules.

2. Typical greenalite granules and their alteration products. No internal structure is visible in these "oölites." Their alteration products are many times as abundant as the unaltered granules, and in many places cannot be distinguished from the alteration product of the kind of structure described under (3).

3. Structures which have the size and outlines of greenalite granules, but whose internal structure is different. They appear to be made up of groups or chains of minute concentric rings which are commonly of chert but may be of a dark graphitic (?) dust or exceedingly minute specks of hematite. Their centers and the matrix in which these rings are imbedded are practically always of the same material, but different from the rings them-

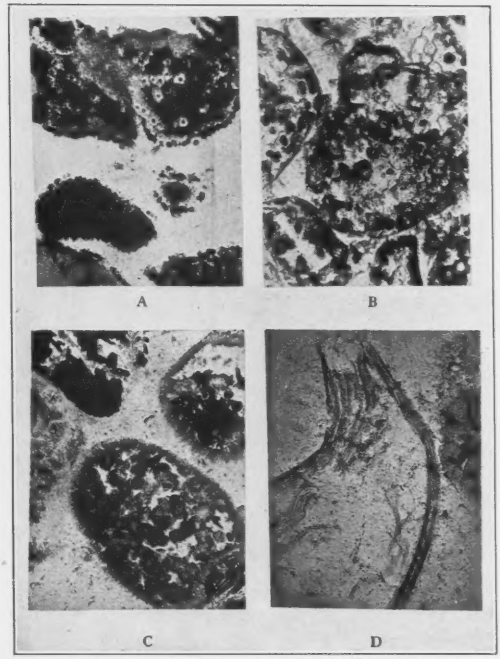
[17] Bucher, W. H., "On Oölites and Spherulites," *Jour. Geol.*, vol. 26, 1918, p. 594.

[18] Schade, H., "Zur Enstehung der Harnsteine und ähnlicher konzentrisch geschichteter Steine organischen und anorganischen Ursprungs," *Zeitschr. Chem. u. Ind. d. Kolloide*, vol. 4, 1909, pp. 175–180, 261–266.

[19] *Op. cit.*, p. 594.

[20] *Op. cit.*, Plate VII., Fig. 2.

[21] *Op. cit.*, Plate XIII., p.



A. Groups and chains of minute concentric rings of chert in granules of greenalite. Matrix of large granules is chert. Nuclei in small rings and surrounding matrix of greenalite-like substance. Some ring structures not visible. × 70.

B. Structures similar to *A*. Chert rings surrounded by "dusty" black rings. Nuclei of same material. Some round dusty black areas without rings. Compare with Pl. VII., *B*. × 70.

C. Large granules (in matrix of chert) with small concentric structures of hematite "dust" and chert. Heavy black areas are magnetite and hematite. Needles of specular hematite cut the concentric structures. Compare with Plate VII., *B*. × 130.

D. Part of structure in Fig. 43. From "algal structure" horizon of Gunflint range. Dark areas in picture are light green. × 170.

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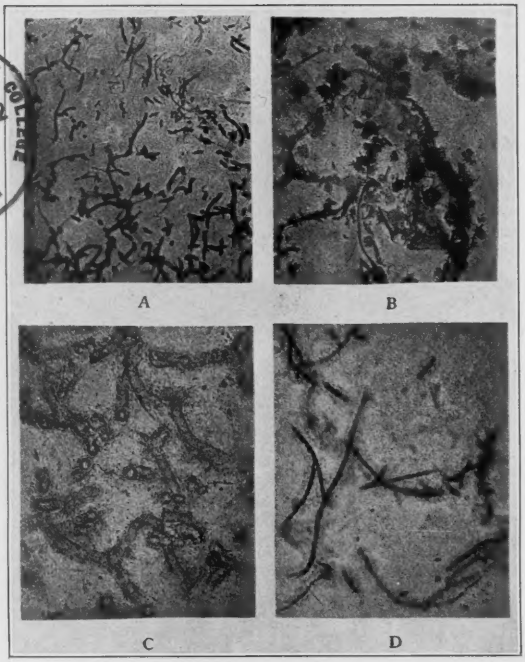


A. Iron bacteria and algæ in chert. Most bacteria outlined by heavy sheaths of brown color. × 65.

B. Another view of *A*. Algæ are prominent. Note resemblance of round structures to those in greenalite structures. (Pl. VI.) Dark colored structures are brown. × 70.

C. Algæ resembling *Microcoleus* (Prof. Josephine Tilden) in chert. Same slide as *A*. Chert and algæ are practically of the same color. × 260.

D. Iron bacteria resembling *Chlamydothrix* from same specimen as algæ in *C*. × 260.

selves. For example, Plate VI., *A* shows chert rings with greenalite centers and matrix. Black centers (probably not magnetite) with a white chert ring and another "dusty" black one around it may be seen in Plate VI., *B*. A somewhat similar structure is that of Plate VI., *C*. In it the dark centers are missing. Spurr[22] noticed these structures and has an excellent illustration of the greenalite phase of them in his report. He thought that they represented a decomposition phase of "glauconite." Leith[23] also illustrates them and says that they suggest organic structures. In the Clinton ores in which similar structures occur, they are "clearly due to the replacement of a shell with regular structure," according to Leith. Wethered[24] shows some similar structures in oölitic limestone, and attributes them to organisms. These minute structures are of remarkably uniform size (0.03–0.04 mm.). Due to the difference in degree of alteration, they may be composed of different minerals as in the larger greenalite structures. The fact that they are preserved only in fine-grained or almost amorphous material, and not in the more crystallized granules, indicates the primary origin of these structures. It is usual to find them penetrated by magnetite, hematite, or amphibole crystals. In places they may form rings around apparently massive greenalite. When such greenalite granules were examined carefully with strong artificial light, it was sometimes noticed that the apparently homogeneous mass showed faint outlines of these minute structures.

About 200 thin sections from the Biwabik and Gunflint ranges were examined; in many of the less altered ones these structures were seen. In most of them (except those from the East Mesabi) at least traces of the structures were preserved. In the light of the other evidence presented on page 419, they are attributed to the work of microörganisms, and may be called cell structures. Unless all of the greenalite granules are made up of cell structures or some other form of organism, we may con-

[22] *Op. cit.*, Plate VI., Figs. 1 and 2.
[23] Mon. 43, p. 117 and Plate XIV., *A* and *B*.
[24] *Op. cit.*, Figs. 5 and 7.

clude that the following conditions probably would be favorable for the formation of granules without internal structure:

1. Relatively rapid deposition of colloidal precipitates.
2. Lack of strong tendency to crystallize, on account of the colloidal character of silica and ferrous and ferric organic compounds and hydroxides.
3. Absence of fragmental grains which could have formed the nuclei of oölites.

Structures Related to Greenalite Granules.

Many iron ore formations show granular structures similar to greenalite, but most of them differ in one respect—that the majority of their granules are true oölites with concentric ring structures. In most of the formations, however, there occur a relatively small number of granules which have not concentric structures, and therefore resemble typical greenalite structures.

In the Wabana oölites[25] other features also are noteworthy. Boring algæ have been found in the oölites, and Hayes thinks it possible that they were active in the production of hematite.

In the Biwabik formation we find hematite and greenalite together. Hematite is commonly taken to be an alteration product of the greenalite. In the Wabana oölites hematite and chamosite occur in alternating concentric rings. It seems fairly certain to the writer that hematite here is not an alteration product of chamosite. It would be difficult to believe that one concentric layer could have remained in one state of oxidation while an adjacent one was changed to some other state, unless there was a conspicuous original difference. There is no reason, then, why hematite (or a *ferric* hydroxide), where associated with greenalite, could not have been an important primary mineral in the Biwabik formation.

The remarkable similarity in shape of the greenalite and Clinton granules has been emphasized by Leith.[26] McCallie[27] describes

[25] Hayes, A. C., "Wabana Iron Ore of Newfoundland," Canada Geol. Surv. Memoir 78, 1915.

[26] Mon. 43, p. 251.

[27] McCallie, S. W., "Report on the Fossil Iron Ores of Georgia," Geol. Surv. Georgia, Bull. 17, 1908, p. 174.

Clinton ore granules with a nucleus of a greenish mineral which he thinks is similar to greenalite.

Glauconite resembles greenalite closely in shape and internal structure. Spurr[28] thought that greenalite is a potassium-poor variety of glauconite. Leith objected[29] to this, because aluminum is also absent from the greenalite, and because detrital mud, always associated with glauconite, is not found with greenalite. It is probable, however, that greenalite granules form by processes similar to those active in the making of glauconite. According to Clarke,[30] this process may be adsorption. So far, however, no generally accepted theory has been advanced for the formation of glauconite.[31]

Microörganisms in and near the Biwabik Formation.

Lower organisms were widespread in Upper Huronian time.[32] In 1911 Cayeux[33] mentioned organic structures in the Mesabi, Menominee, and Penokee Gogebic ranges, but his work is not clear as to what structures were meant.

In the present investigation, specimens of chert which contain

[28] *Op. cit.*, p. 242.

[29] *Op. cit.*, pp. 242 and 254.

[30] *Op. cit.*, pp. 513–514.

[31] Murray, J., and Renard, A. F., "Voyage of the Challenger; Deep Sea Deposits," 1891, p. 389.

Murray, J., and Hjort, J., "Depths of the Ocean," London, 1912, p. 189.

Collet, L. W., and Lee, G. W., "Recherches sur la galuconie," *Proc. Roy. Soc. Edinbg.*, vol. 26, 1906, pp. 259–262.

Andree, K., "Über Sedimentbildung am Meeresboden," *Geol. Rundschau*, vol. 8, 1917, pp. 59–61.

[32] Walcott, C. D., "Pre-Cambrian Algonkian Algal Flora," Smiths. Inst. Misc. Coll., vol. 64, no. 2, 1914.

Idem, "Notes on Fossils from Limestone of Steeprock Lake, Ontario," Geol. Survey Canada, Mem. 28, 1912, p. 16.

Moore, E. S., "The Iron Formation on Belcher Islands, Hudson Bay, etc.," *Jour. Geol.*, vol. 24, 1918, pp. 412–438.

Grout and Broderick, *Am. Jour. Sci.*, vol. 48, 1919, p. 199.

Broderick, T. M., ECON. GEOL., vol. 15, 1920, p. 422.

[33] Cayeux, L., "Existence de restes organiques dans les roches ferrugineuses associees aux minerais de fer huroniens des Etats-Unis," *Compt. rend.*, vol. 153, 1911, pp. 910–912.

not only algæ, but also iron bacteria and most probably bacilli (Plates VII. and VIII.) were found. The chert was found in the Archean greenstones and the Lower Middle Huronian graywackes northeast of Eveleth. Cherts of gray, greenish, and jasper-red tints fill joint cracks of varying widths in the greenstone and graywacke. In places the cracks widen out into larger irregular areas. Often these cracks are straight for 6 to 10 feet. They must have been filled after the last severe folding of the area. This folding took place before the laying down of the iron-bearing formation. Glacial erosion has planed off weathered material and has left a smooth, almost fresh, surface of greenstone and graywacke. That the organisms are at least as old as the Upper Huronian rocks seems to be evident from the following observations:

1. The chert is fresh, and indistinguishable, either in the hand specimen or under the microscope, from any of the cherts of the Lake Superior region.

2. Under the microscope it is seen to be finely crystalline and to contain small perfect rhombohedral crystals of carbonate, as in iron carbonate of the iron-bearing rocks.

3. Microscopic needles of an amphibole, probably actinolite, are observed in the chert. These needles are common in the iron-bearing formations, and indicate considerable depth of burial.

4. Minute pyrite cubes replace the chert, and in one place, the algal growths also. Pyrite is abundant throughout the greenstones and graywackes[34] in this area. It probably was introduced during or at the end of the last intrusive activity, which, in this area, seems to be represented by a porphyry dike containing pyrite only a few hundred feet away from the place at which the organisms were found. This dike was assigned to the Keweenawan period by the writer.[35] In the cherty phases of the Biwabik formation pyrite is almost absent. It seems reasonable to infer, then, that the pyrite associated with the microörganisms was introduced hydrothermally.

[34] Van Hise and Leith, *op. cit.*, p. 512.

[35] Report in preparation.

5. The chert filling the cracks in the greenstone and graywacke is found only within 1,800 feet of the present edge of the Biwabik formation; farther away there is none. If the dip of the Biwabik formation be projected toward the greenstone, it is found that the fossils would be only a very short distance, if any, below the bottom of the former iron-bearing sediments. The Pokegama quartzite is thin in this area, and probably was almost absent in some places. This would mean that the iron-bearing formation practically rested on the Archean or Lower Middle Huronian rocks, as it does in some other places on the range.

6. No chert later than that of the Biwabik formation has ever been reported from the Lake Superior region. On the other hand, the chert is removed in enormous quantities from the ore. Where silica has been redeposited in veins, it has been in the form of quartz. As a matter of fact, in one place small quartz veins were found which cut the chert in the joint cracks. If this chert, however, were really deposited by descending solutions, it would be, so far as the writer knows, the first fossiliferous chert observed in true veins.

7. The chert is embedded in country rock which seems to be practically fresh at the contacts, as if it had not been exposed to weathering. It is probable that the massive, already metamorphosed, rock protected the chert in the joint cracks from deformation and changes experienced by the Biwabik formation proper.

8. According to Grout,[36] on the East Mesabi Range fissures in granite are filled with rock of the iron-bearing formation which overlies the granite. Cases are also known in which chert and jasper filling joint cracks in greenstone and basalt are associated with overlying cherts and iron-bearing formations.[37]

In studying the algæ of Plate VII., *B* and *C* and thin sections of other specimens from the same locality, it was observed that there seems to exist a gradation from the perfect ones (which form a

[36] Personal communication.

[37] Leith, C. K., "An Algonkian Basin in Hudson Bay—a Comparison with the Lake Superior Basin," ECON. GEOL., vol. 5, 1910, p. 242.

Dewey, H., and Fleet, J. S., "On Some British Pillow-lavas and the Rocks Associated with Them," *Geol. Mag.*, vol. 48, 1911, pp. 202–209, and 241–248.

network) to groups which seem to consist only of concentric rings, or round spots (like some in Plate VII., *B*) without any connecting portions or sheaths between them. These simpler rings or spots usually seem to be a little larger than the cross sections of the algæ in Plate VII., *C*. They resemble the rings in the greenalite structures (Plates VI. and VIII., *A*) very much, and strongly suggest a relation in origin.

New organisms were also found in the cherts of the algal structure horizon of the Gunflint and Biwabik formations. Bacilli (there is little doubt that they are such) of the same kind as those shown in Plate VIII., *B* were found in two specimens from the algal structures of the Upper Cherty Division near Hibbing. They are of the same shape and size as those in Plate VIII., *B*, but are less numerous. According to Professor A. T. Henrici,[38] they are probably the same species.

In this connection may be mentioned rods of silica (about 10 to 12 microns long) which were observed by Bleicher[39] in oölites of the Minette ores of France. These rods are said to resemble bacteria. In a specimen from the algal structure horizon of the Upper Cherty Division on the Gunflint Range, the algæ shown in Fig. 43 and in Plate VI., *D* were found. There still exists some doubt as to whether these plants belong to a higher class than algæ. Microörganisms, probably fungi and algæ, were also found by the writer in chert pebbles of the basal conglomerate of rock assigned by Leith[40] to the Pokegama quartzite. Lack of space prevents their being described here. They corroborate, however, the evidence that the algæ and bacteria described in the preceding paragraphs are of at least Upper Huronian age.

The writer wishes to express his thanks to Dr. C. D. Walcott and to Dr. Albert Mann, of the Smithsonian Institute, for examining one of the sections containing fungi-like plants, to Professor Josephine Tilden, Professor C. O. Rosendahl, and Profes-

[38] Dept. of Bacteriology, Univ. of Minnesota.

[39] Quoted by Van Werweke, L., "Bemerkungen über die Zusammensetzung und die Enstehung der lothringisch-luxemburgischen oolithischen Eisenerze," *Zeitschr. prak. Geol.*, vol. 9, 1901, p. 396.

[40] *Op. cit.*, Mon. 43, p. 97.

sor F. K. Butters, of the department of Botany of the University of Minnesota, for the identification of algæ and similar structures, and to Professor A. T. Henrici for identification of the bacteria. Professor Charles Schuchert of Yale University also had the kindness to examine the photographs.

SOLUTION OF IRON AND SILICA.

In the following experiments an attempt has been made to show that iron and silica are dissolved by solutions from decaying organic matter. The results have been compared with those obtained in experiments with carbonated water and with other dilute acid solutions.

Amounts of Iron in Natural Waters.

The average river water contains less than one part per million of iron.[41] Sea waters also are very low in iron. This suggests that such waters are an inadequate source for the deposition of a great iron-bearing formation. There are, however, some analyses showing more iron. The rivers of Brazil and other parts of South America carry from 2 to 7 parts of Fe_2O_3; this is a relatively large percentage of their total mineral content, which is usually low.[42]

Swamp waters commonly contain more iron than other surface water.[43] Moore[44] reports three waters with 47 to 61 parts of Fe_2O_3 per million, either from lakes in which iron ores are in the process of formation, or from creeks tributary to such lakes.

[41] Clarke, F. W., "The Data of Geochemistry," U. S. Geol. Survey, Bull. 695, 1920.

[42] Clarke, F. W., *op. cit.*, pp. 90–92. See also analyses *B* and *E*, p. 77; *G*, p. 93; and *E*, p. 105, which contain unusual amounts of iron and organic matter.

[43] Endell, K., "Der Säuregehalt des Moorwassers," *Jour. prakt. Chem.*, vol. 82, pp. 414–422, 1910.

See also Endell, K., "Über die chemische und mineralogische Veränderung basischer Eruptivegesteine bei der Zersetzung unter Mooren," *Neues Jahrb. Min.*, Beilage Bd. 31, 1911, pp. 1–54.

[44] Moore, E. J., "The Occurrence and Origin of Some Bog Iron Deposits in the District of Thunder Bay, Ontario," Econ. Geol., vol. 5, 1910, pp. 528–538.

Simpson[45] mentions a small stream which contains 17 parts per million of iron and much organic matter. It is noteworthy that organic matter seems to be always present in surface waters that contain much iron.

Spring waters often carry iron, but such waters are probably not the sources of the large iron-bearing formations, on account of their limited quantity.

Decaying Organic Matter as Solvent.

From decaying plant life there may be extracted by water a brownish solution which is, for the most part, colloidal in nature.[46] These solutions are slightly acid, but it is not known yet whether this acidity is due to so-called "humus acid"[47] (which is an indeterminate substance), or to other organic or inorganic acids, such as carbon dioxide.[48]

With such solutions,[49] it is thought that iron can form so-called ferrous and ferric humates, which probably are colloidal in nature and, under certain conditions, retain iron persistently. In 1870 Thenard[50] stated that silica could form "silico-azo humic acids" with humus and nitrogen. Julien[51] based some of his conclu-

[45] Simpson, E. S., "Notes on Laterites in Western Australia," *Geol. Mag.*, vol. 49, 1912, p. 405.

[46] Clarke, F. W., *op. cit.*, p. 106.

Odén, Sven, "Die Huminsäuren. Chemische, physikalische und bodenkundliche Forschungen," *Kolloidchemische Beihefte*, vol. 11, 1919, p. 104.

Albert, R., "Bemerkungen zu den Abhandlungen von H. Stremme über die 'so-genannten Humussäuren,'" *Zeitschr. prakt. Geol.*, vol. 17, 1909, p. 528.

Stremme, H., "Die so-genannten 'Humussäuren,'" *Zeitschr. prakt. Geol.*, vol. 17, 1909, pp. 353–355.

Gillespie, L. J., and Wise, E., "Action of Normal Salts on Humus and Other Experiments on Soil Acidity," *Jour. Am. Chem. Soc.*, vol. 40, 1918, p. 796.

Aschan, O., "Die Bedeutung der wasserlöslichen Humusstoffe für die Bildung der See und Sumpferze," *Zeitschr. prakt. Geol.*, vol. 15, 1907, p. 57.

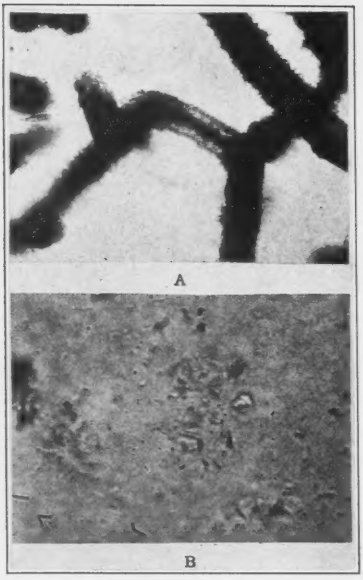
[47] Odén, Sven, *op. cit.*, pp. 138 and 147.

[48] Van Hise, C. R., "A Treatise on Metamorphism," U. S. Geol. Survey Mon. 47, 1904, p. 461.

[49] Odén, S., *op. cit.*, p. 180.

[50] Thenard, P., *Compt. Rend.*, vol. 70, 1870, p. 1412.

[51] Julien, A. A., "On the Geological Action of the Humus Acids," *Am. Assoc. Adv. Sci.*, vol. 28, 1879, pp. 311–410.



A

B

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A. Iron bacteria from the same specimen as in Plate VII. Note sheath and cross section of sheath in upper right corner. Black areas brown in specimen. × 1300.

B. Bacilli from the same specimen as *A*. Minute rods rounded at the ends; some are bent; uniform in size and numerous. Only a few can be got into focus at one time. They are white like the chert. × 1300.

sions on the existence of these "acids." Clarke,[52] however, discredited Thenard's statement. Niklas,[53] in the study of soils, has demonstrated the solubility of minerals and rocks in peat solutions. Weiss[54] has shown that peat solutions will change an impure clay to a residue of almost pure kaolin.

Experiments with Peat Solutions.

Material Used and Methods of Analysis of Solutions.—In all experiments distilled water and the same kind of a lime-deficient peat from William's bog north of Duluth, Minnesota, were used. A partial analysis of the peat (after drying at 110° for 5 hours) gave:

	Per Cent.		Per Cent.
Total ash	7.110	CaO	0.510
SiO_2	5.660	MgO	0.360
Fe	0.012		

Mineral and rock powders (ground in agate mortar) that passed through 200 mesh were used. Glauconite sand was used without powdering it. In all experiments with a certain mineral or rock, powder from the same crushed sample was taken. Determinations of silica and iron were made of most samples. A list of the minerals and rocks used follows:

1. *Pyrite*—crystals with possibly a little quartz. Washed with dilute HCl.
2. *Hematite*—compact columnar variety. It was used in preference to specular hematite, as the latter seems to be mixed with magnetite, as a rule. The powder in water was cleaned with a magnet. No magnetic particles were found.
3. *Limonite*—reniform. Contains some SiO_2. Treated like hematite. Washed with dilute HCl to free from any carbonate.

[52] *Op. cit.*, p. 106.

[53] Niklas, H., "Untersuchungen über den Einfluss von Humusstoffen auf die Verwitterung der Silikate," *Int. Mitt. f. Bodenkunde*, vol. 2, 1912, pp. 214–244.

[54] Weiss, F., "Vorkommen und Entstehung der Kaolinerden des ostthürgingeschen Buntsandsteinbeckens," *Zeitschr. prakt. Geol.*, 1910, p. 365.

4. *Siderite*—massive, crystalline with some quartz. CaO trace; MgO 4.5.
5. *Magnetite*—from Port Henry, N. Y. Massive variety.
6. *Augite*—black massive variety with a little calcite. Powder was cleaned under water with a strong magnet. SiO_2 38.6; Fe 14.06.
7. *Olivine rock*—granular, from Scott's creek, Jackson County, N. C. Washed and treated magnetically to extract any magnetite. SiO_2 41.9; Fe 4.99.
8. *Serpentine*—massive yellowish green variety. Apparently contains no other mineral. SiO_2 41.8; Fe 3.57.
9. *Glauconite sand*—from New Jersey.
10. *Greenalite rock*—Mesabi Range, Section 19, T. 57 N., R. 21 W. Greenalite granules are conspicuous. SiO_2 46.40; Fe 16.27; CaO 2.96; MgO 26.20.
11. *Magnetic ferruginous chert*—Mesabi Range, Section 27, T. 56 N., R. 24 W. Contains about 20 per cent. of iron as magnetite and a little carbonate (no calcite). SiO_2 44.09; Fe 29.39.
12. *Ely greenstone*—spherulitic. Near Ely, Minnesota. SiO_2 45.3; Fe 10.69.
13. *Duluth gabbro*—dark variety. Near Duluth, Minnesota. SiO_2 54.93; Fe 10.02.
14. *Sudbury nickel ore*—norite, pyrrhotite, and pentlandite. Pyrrhotite makes up 70 or more per cent. of specimen.

The solutions, after having been in contact with the mineral matter the required time, were filtered and evaporated in pyrex beakers to 50 c.c., then in platinum dishes; and the organic matter was burned off. The residue was analyzed by standard methods (silica by hydrofluorizing, iron by titration with potassium permanganate). When only approximate results were desired, as in Table III., colorimetric estimates were made. Potassium ferricyanide in excess was added to the organic solution, and the color of the latter was compared with another organic acid solution of known iron content, to which the same amount of potas-

sium ferricyanide had been added. Quantitative check analyses showed this to give good results.

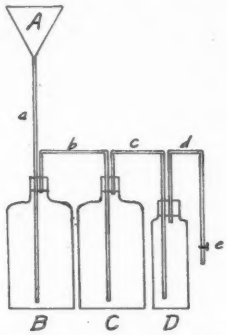

FIG. 44. Apparatus used in the solution of minerals by peat waters.

Action on Powdered Mineral Matter.—The apparatus shown in Fig. 44 was used to assure a large and continuous supply of solution from the different minerals. The stoppers and connections between the glass tubes and funnels were of rubber. 20 grams of the mineral were mixed with as much peat as could be conveniently put into bottle (*B*) without stopping the circulation of water. 15 grams of the same mineral were put into bottle (*C*) with distilled water and allowed to settle. Flask (*D*) was filled with distilled water and was intended to catch any solid particles that might come over from bottle (*C*). Funnel (*A*) was filled with peat, and in order to keep the peat from entering tube (*a*), glass-wool was placed in the bottom of (*A*). The whole apparatus was then filled by letting the air slowly escape through the stopcock (*e*) and pouring distilled water into the funnel. Then 500 c.c. of solution were drawn off each week through stopcock (*e*). For each of the minerals and rocks mentioned, except serpentine, and for a blank, the apparatus and conditions for the experiment were identical.

While it was expected that the peat solution would dissolve all the mineral matter it could hold in bottle (*B*), the vessel (*C*)

was introduced in order to have the solution also come into contact with mineral matter in the absence of peat. This would correspond to natural conditions, where the peat solutions percolate through underlying rocks, and, according to some geologists, deposit a part of the salts they contain. Considerable amounts of gas were observed to collect in the bottles about two weeks after they were filled, and continued to form to the end of the experiments. It was probably a mixture of hydrocarbon gases, as some of it was inflammable. The amount of organic matter in different solutions varied greatly. The maximum amount observed was 317 parts of organic matter (dried at 105°) per million.

As the peat solution slowly rose in bottle (*C*) when the water was drawn off at (*e*), a relatively sharp line was observed at the contact of the solution with the distilled water. The colloidal solution evidently did not diffuse in the water above it to an appreciable extent. The solutions were clear, though ranging in color from yellow to dark brown. All the peat solutions, unless the contrary is stated, reacted either slightly acid or neutral, with litmus solution or neutral red as indicators.

Not all the minerals gave up iron with the same rapidity. The pyrite, magnetite, siderite, magnetic ferruginous chert, greenstone, augite, olivine, and Sudbury ore solutions contained iron when the peat water first reached the outlet of the apparatus (after 40 days). The solutions from greenalite and Duluth gabbro gave tests for iron 20 days later, while iron did not appear from hematite, limonite, and glauconite until 30 days after the peat water had reached the outlet. This is probably due to the fact that iron is contained in these last three minerals in the ferric state, which requires more time for solution, on account of the necessary reduction to the ferrous condition.

Qualitative tests for iron (which was always in the ferrous state) were made with potassium ferricyanide. Colloidal iron does not react with potassium ferro- and ferricyanide,[55] for this reaction takes place between the ions. Since tests with the cya-

[55] Zsigmondy, R., "Kolloidchemie," 1918, p. 270.

nides showed ferrous iron, we know that the iron is present in part in true solution. Dialysis of one of the solutions through a collodion membrane showed that Fe ions were abundant, though colloidal ferro-humates may have been present also. Alumina seemed to be present in traces only, according to qualitative tests. The partial analyses of two samples of 500 c.c. each, taken at intervals of about 80 and 170 days respectively, are given in Table I.

TABLE I.

SOLUBILITY OF MINERALS AND ROCKS IN PEAT SOLUTIONS.
(Parts per Million.)

	After 77 Days.		After 182 Days.			
	SiO_2.	Fe.	SiO_2.	Fe.	CaO.	MgO.
Blank	1	Trace	6	2	9	Trace
Pyrite	Not det.	23	9	14	7	Trace
Hematite	Some	25	10	27	8	Trace
Limonite	Some	14	15	30	7	Trace
Magnetite	Not det.	31	8	41	10	Trace
Siderite	Some	94	10	48	9	Trace

	After 90 Days.		After 165 Days.			
	SiO_2.	Fe.	SiO_2.	Fe.	CaO.	MgO.
Augite	40	9	35	8	31	2
Olivine	161	14	106	9.5	8	24
Greenstone	81	20	68	15	16	Trace
Duluth gabbro	78	19	82	15	16	Trace
Greenalite rock	47	17	44	9	8	2
Magnetic ferrug. chert	30	27	33	25	14	2
Glauconite sand	26	15	35	19	29	3
Sudbury ore	25	22	30	16	14	Trace

Some experiments were performed to ascertain the reaction of peat solution on minerals under static conditions. Glass bottles of a volume of 2,500 c.c. were filled with 20 grams of the mineral, about 75 grams of peat, and distilled water. Then they were closed with greased glass stoppers. Occasionally they were shaken. After 120 days, 500 c.c. of each solution were analyzed (Table II.).

TABLE II.

SOLUBILITY OF MINERALS AND ROCKS IN PEAT SOLUTIONS IN 120 DAYS.
(Parts per Million.)

	SiO_2.	Fe.	CaO.	MgO.
Blank	3.2	Faint trace		
Magnetite	9.0	26.0		
Siderite	10.0	29.1		
Pyrite	Not det.	Trace		
Serpentine*	83.0	4.0	Trace	24.0
Orthoclase	23.0	None	None	
Labradorite	25.0	None	Trace	

* Serpentine: Ratio of SiO_2 to Fe in Mineral ..... 11.7 : 1
Ratio of SiO_2 to Fe in Solution ..... 21.0 : 1

From Tables I. and II., it will be seen that pyrite did not go into solution when no circulation existed, and that relatively little was dissolved after 182 days, even in circulating solutions. This is seen by the decrease of iron from 23 to 14 parts in 105 days. Magnetite is, next to siderite, most easily attacked. Siderite seems to be subject to great fluctuations. It is possible that the decrease in its solubility is due partly to the presence of magnesia in the iron carbonate. Limonite and hematite are attacked slowly at first, but more rapidly later.

TABLE III.

SOLUBILITY OF MINERALS IN PEAT SOLUTION IN CONTACT WITH AIR, AFTER 30 DAYS.
(Parts per Million.)

	SiO_2.	Fe.
Augite no. 6	51.6	6.0
Olivine	239.0	8.0
Serpentine	88.4	Trace
Magnetic ferrug. chert	35.0	11.0
Orthoclase	18.8	Faint trace
Pyrite		Trace
Hematite		Trace
Limonite		Trace
Magnetite		Trace
Siderite		15+ (colorimet. estimate)

To determine the solubility of iron and silica in peat solutions

in contact with air, wide-mouthed 500 c.c. bottles were filled with 10 grams of peat, 3 grams of the mineral matter, and distilled water. The solutions were agitated once a week. After 30 days they were analyzed with the results given in Table III. Iron is dissolved in smaller quantities in the solutions in the presence of air. It could be detected in some with potassium ferri- or ferrocyanide, only after adding hydrochloric acid. It is possible that these small amounts were in the colloidal state. Silicates, especially those rich in magnesium, seem to be broken up with ease by all peat solutions.

In this connection, attention is called to similar results obtained by Niklas.[56] It is believed, therefore, that as a rule, the lower the percentage of silica in the silicate, the higher the content of silica in solution. Low SiO_2 means larger amounts of MgO and CaO in the minerals like olivine and augite, respectively, and it will be noticed that solutions of such minerals seem to contain little iron. Yet on closer inspection it is found that the ratio of SiO_2 to Fe in the minerals and rocks is very similar to that of SiO_2 to Fe in the solutions. An exception to this is serpentine, in which nearly twice as much SiO_2 is in solution as would be expected from the ratio of SiO_2 to Fe in the mineral. This solution was neutral to litmus.

Easily soluble minerals like calcite, olivine, and serpentine, reduce the acidity of solutions.[57] But the less acid the solution, the less iron will be dissolved. It is highly probable that a little iron can be adsorbed by the organic colloids and carried in this manner, even in neutral solutions.

There remains to be accounted for the extremely low percentage of MgO and CaO in general in the peat solutions. We can hardly assume that silica and iron would be leached from a mineral, leaving a skeleton of MgO, CaO, and Al_2O_3. The silica set free is in solution as a colloid. The iron is in the ionic or colloidal state, and Al_2O_3 is precipitated immediately or does not

[56] *Op. cit.*

[57] Nishihara, G. S., "The Rate of Reduction of Acidity of Descending Waters by Certain Ore and Gangue Minerals and Its Bearing upon Secondary Sulphide Enrichment," ECON. GEOL., vol. 9, 1914, pp. 743–757.

go into solution at all; MgO and CaO, on the other hand, while dissolved, are adsorbed by the colloids of the peat,[58] or precipitated as organic compounds, and appear in the solutions in only small amounts. The amount of silica in the solutions from olivine is greater in the presence of air than in the absence of air.

The following experiments indicate that the efficiency of peat solutions alone is practically as great as that of peat solutions in contact with the peat. The minerals tested in filtered peat solutions were siderite, pyrite, hematite, limonite, and magnetite. One gram of each was put into a large test tube (75 c.c.), and filtered peat solution from the blank sample of the first experiment (Table I.) was added. The full tubes were closed with rubber stoppers. Colorimetric estimations of iron after 45 days gave results similar to those of Table I.

In order to find out whether a mineral such as serpentine, due to its easy solubility and basic character, could influence the solubility of the iron oxides in a marked degree when mixed with them, three experiments were made. To three bottles of 2,500 c.c. capacity each, containing distilled water, 20 grams of peat, and 10 grams of serpentine, were added: (1) 10 grams of siderite, (2) 10 grams of limonite, and (3) 10 grams of magnetite. The water present was sufficient to fill the bottles. They were stoppered and agitated a little about every two days. The analyses after 45 days showed, in parts per million:

		SiO_2.	Fe.
(1)	Serpentine + siderite	60.5	24.7
(2)	" + limonite	68.9	29.0
(3)	" + magnetite	83.2	15.7

In the case of siderite and limonite, the amount of iron is a little smaller than in the absence of serpentine. In the case of magnetite, only about half as much iron, on an average, has gone into solution as in the absence of serpentine.

Action on Polished Surfaces and Thin Sections.—Polished pieces of magnetite, pyrite, magnetite and hematite together in one specimen, and magnetite, chert, and carbonate together in

[58] Clarke, F. W., *op. cit.*, p. 497.

another specimen, were submerged in stoppered bottles that contained peat and water. The bottles were carefully stoppered. After two months all the solutions contained at least traces of iron. The magnetite and hematite had lost some of their luster, while the pyrite was practically unaffected. In the specimen that contained magnetite, chert, and carbonate, the carbonate had been eaten out to appreciable depth, leaving the other minerals unchanged.

Thin sections of Mesabi taconite (chert with granules of hematite), basalt, gabbro, olivine gabbro, hornblende schist, quartz diorite with biotite, and opal were treated as follows: For each slide an apparatus similar to Fig. 44 was used. Half of the cover glass and Canada balsam of each slide was removed, and the slide put into a bottle which would correspond to bottle (*C*) in Fig. 44. The slide was thus not in contact with peat. About 500 c.c. of solution were drawn off every month. After seven months the slides were examined.

In the taconite the hematite contained in the granules had been partly dissolved. In the olivine gabbro, the olivine in the uncovered portion had been either changed to an almost isotropic substance with an index of 1.552, or had been "eaten out" entirely in a few places. The resemblance of the remaining portions to serpentine is great in index and birefringence. Augite, which was also present in the olivine gabbro, was not altered noticeably. In the other slides only slight clouding was observed.

Combinations of Peat and Salt Solutions.

Colloids or very porous substances, when brought into contact with solutions of neutral salts, commonly adsorb the base-forming element, causing the solutions to become acid.[59] Many experi-

[59] Cameron, F. K., and Bell, J. M., "The Mineral Constituents of the Soil Solution," U. S. Dept. Agr. Bur. of Soils, Bull. 30, 1905, p. 39.

Sullivan, E. C., "The Interaction between Minerals and Water Solutions with Special Reference to Geologic Phenomena," U. S. Geol. Survey, Bull. 312, 1907, p. 10.

Harris, J. E., "Some Adsorption Phenomena in Soils and Kaolin," *Jour. Phys. Chem.*, vol. 18, 1914, pp. 355–371.

Bancroft, W. D., "Applied Colloid Chemistry," New York, 1921, pp. 90–128.

Clarke, F. W., *op. cit.*, p. 496.

ments were made by the writer to determine the effect of adsorption by peat solutions. Peat and powdered mineral matter were added to a salt solution. A few of the results are given in Table IV. They clearly indicate that strong acids were liberated in the case of sulphate and chloride solutions. These acids attacked the minerals much more than the ordinary peat solutions (Table I.). In the solutions containing carbonates, on the other hand, only carbonic acid was freed. This was shown by strong effervescence when the bottles were opened. The carbonic acid attacked the minerals relatively feebly. The solutions with the chlorides and sulphates were almost colorless and contained very little organic matter; those with the carbonates were brownish yellow and had much organic matter. The solubility of iron and silica in the presence of air was similar to that in its absence, in these solutions. When mineral matter and a salt were added to a *filtered* peat solution, very similar results were obtained. The uniformity in the amounts of iron in the vessels containing $CaCO_3$ (Table IV.) seems to indicate that the combination of

TABLE IV.

SOLUBILITY OF IRON AND SILICA FROM MINERALS IN SALT SOLUTIONS IN CONTACT WITH PEAT IN CLOSED BOTTLES FOR 40 DAYS.
(Parts per Million.)

½ G. of Peat and ½ G. of Mineral in 75 c.c. Sol.		Kind and Concentration of Salt Used in 75 c.c. Distilled Water.				
		1½ G. Na_2SO_4.	1½ G. NaCl.	1½ G. $MgCl_2$.	½ G. $MgCO_3$.	½ G. $CaCO_3$.
Pyrite	Fe	333.8				
Magnetite	Fe	157.8				
Olivine	Fe		22.4*	36.1		8.4
	SiO_2		132.4	121.2		57.1
Greenalite	Fe					8.4
	SiO_2					33.1
Magnetic ferruginous chert	Fe				5.1	8.7
	SiO_2				12.0	26.6
		Solutions acid†			Sol. alkal.	Sol. neutral

* 224.0 parts MgO in solution.
† Litmus for indicator.

water, peat, and $CaCO_3$ cannot hold more than 8.5 to 9.0 parts of iron per million in solution.[60]

Artificial sea water[61] was used with peat in two experiments. After 135 days (in closed bottles) the solutions contained, in parts per million:

	From Greenstone.	From Serpentine.
SiO_2	18.0	111.2
Al_2O_3	3.2	——
Fe	124.0	13.0

All iron was in the ferrous state.

Sea water alone and sea water with greenstone after 135 days contained only traces of iron and silica.

This behavior of decaying plant life when acted on by sea water or other chlorides and sulphates is, it seems to the writer, of great geologic importance. Possibly an indication that decaying animal tissue brings about similar reactions is the statement by Murray and Irvine[62] that putrifying mussel flesh in sea water is able to dissolve 25 parts of silica per million from diatom and globigerina oozes.

Carbonated Water as Solvent.

A few experiments were made with carbonated water, and the results were compared with those of former experiments.[63] Flasks (500 c.c.) were filled with distilled water as nearly satu-

[60] The solutions from augite, which contains calcite (Tables I. and III.), also have not more than 9 parts of iron.

[61] The solutions contained per liter:

$MgCl_2 \cdot 6H_2O$	8.00 grams	$MgSO_4 \cdot 7H_2O$	3.30 grams
NaCl	27.20 "	$CaSO_4 \cdot 2H_2O$	1.50 "

[62] Murray, J., and Irvine, R., "On Silica and Siliceous Remains of Organisms in Modern Seas," *Proc. Roy. Soc. Edinburgh*, vol. 18, 1891, p. 248.

[63] Müller, R., "Untersuchungen über die Einwirkung des kohlensäurehaltigen Wassers auf einige Mineralien und Gesteine," *Thermaks Min. Mitteil.*, 1877, pp. 25–48.

Henrich, F., "Über die Einwirkung von kohlensäurehaltigem Wasser auf Gesteine und über den Ursprung und den Mechanismus der kohlensäureführenden Thermen," *Zeitschr. prakt. Geol.*, vol. 18, 1910, pp. 85–94.

Leitmeier, H., "Zur Kenntniss der Karbonate," *Neues Jahrb.*, Beil. Bd. 40, 1916, pp. 681–684.

rated with CO_2 as possible, and 5 grams of the mineral matter were added. The flasks were quickly stoppered and sealed. After seven weeks the solutions were analyzed, with the following results:

TABLE V.

MATERIAL DISSOLVED IN WATER SATURATED WITH CARBON DIOXIDE IN 7 WEEKS.
(Parts per Million.)

From	SiO_2.	Fe.	CaO.	MgO.
Siderite*		19.1	Trace	46.0
Magnetite		28.0		
Olivine	44.7	28.9		105.0

* Siderite contains 3.3 per cent. MgO and traces of CaO and SiO_2.

In order to ascertain whether a continuous stream of carbon dioxide would be more effective, 5 grams of each mineral were put into bottles and washed CO_2 was bubbled through the bottles for 2 and 4 weeks respectively.

Special precautions were taken to avoid contamination by air. 50 c.c. of each solution were analyzed each time. The results are given below:

TABLE VI.

MATERIAL DISSOLVED IN WATER THROUGH WHICH CO_2 WAS PASSED CONTINUOUSLY.
(Parts per Million.)

From	After 2 Weeks.				After 4 Weeks.			
	SiO_2.	Fe.	CaO.	MgO.	SiO_2.	Fe.	CaO.	MgO.
Siderite*		29.4		21.0		37.3		89.0
Olivine	61.0	49.7	Trace	235.0	92.0	34.3	Trace	229.0
Duluth Gabbro	14.0	14.0			23.0	26.1	149.0	64.4

* Siderite contains 3.3 per cent. MgO and traces of CaO and SiO_2.

These experiments show that siderite containing some MgO does not go into solution in carbonated water more readily than the silicates or magnetite. The experiments, furthermore, show that more silica and magnesia and less iron was dissolved from olivine

than in similar experiments by Müller and Leitmeier.[64] A continuous stream of carbon dioxide was more effective in attacking magnesia, as might have been expected, but it also dissolved more silica.

Conclusions.

From these experiments[65] the following conclusions may be reached:

1. Solutions from decaying plants dissolve all oxides and carbonates of iron, and most of the silicates, but do not seem to attack pyrite appreciably.

2. The strength of such solutions is similar to that of carbonic acid. It is possible that carbonic acid is the chief acid of the so-called "natural organic acids," but the organic colloids in such solutions give special properties to them.

3. One of the differences between natural organic solutions and carbonic acid is that the organic solutions reduce ferric iron compounds to soluble ferrous salts, while carbonic acid does not.

4. When a solution of a neutral salt with a strong acid radical comes into contact with natural organic colloids, acid is set free which dissolves much iron and silica.

5. The presence of carbonates impedes the solution of silica and iron in natural organic solutions.

6. Ordinarily the ratio of iron to silica in peat solutions in the absence of air (Table I.) is very similar to the ratio of iron to silica in the undecomposed minerals.

The following conclusions, which are of particular value in the study of lateritic deposits, apply to all dilute acid solutions:

7. As a general rule, the less silica a silicate contains, the greater will be the amount of silica dissolved by a given amount of dilute acid.

8. Magnesium salts, in general, accelerate the solution of silica, but impede that of iron.

9. For a similar reason an acid will not extract as much iron

[64] *Op. cit.*

[65] Other experiments by the writer not included in this paper corroborate the conclusions.

from a mixture of a basic silicate (serpentine) and an iron oxide, as from the iron oxide alone.

PRECIPITATION OF IRON AND SILICA.

Precipitation of Iron.

Harder[66] has summarized the precipitation of iron. He says that iron may be precipitated as some form of ferric hydroxide, as basic sulphate, as normal carbonate, as sulphide, or as silicate.

The following observation was made on the solutions which contained iron bicarbonate in the experiments recorded on pages 433 and 434. Three days after the bottles had been opened, all the iron was precipitated as hydroxide, though there had been no agitation of the solutions. This throws doubt on the assumption that iron is carried largely as bicarbonate in surface waters. Spring waters containing much CO_2, however, do carry considerable iron as bicarbonate.

Experiments with Filtered Peat Solutions.—Peat solutions which had taken up iron, after they had been filtered, held the iron in solution in the absence of air without any tendency to precipitation. Even if air had access to the solutions, the precipitation of iron did not begin immediately and did not become complete during one year. Bubbling air through a solution for twenty-four hours had no visible effect on the solution, and did not oxidize the iron. Drying up of a solution produced dark brown, shiny, brittle solids. A large part of this solid could be dissolved again in distilled water. Iron, probably a ferric colloidal compound, was present in the material redissolved. The addition of clean sand or finely-powdered chalcedony or orthoclase did not accelerate precipitation of iron from any of the solutions.

The following experiments show the influence of the addition of carbonates and sulphates: Large test tubes were filled with solutions containing iron which had been drawn off from the large apparatus shown in Fig. 44. Small amounts of the salts

[66] Harder, E. C., "Iron-depositing Bacteria and their Geologic Relations." U. S. Geol. Survey, Prof. P. 113, 1919, pp. 64–84.

TABLE VII.

EFFECT OF CARBONATES AND SULPHATES ON PEAT SOLUTIONS CONTAINING IRON IN STOPPERED BOTTLES.

Minerals from which Peat Solutions Had Dissolved Iron.	Salts Added to 75 c.c. of Solution to Precipitate the Iron.														
	0.1 g. $MgCO_3$.			0.1 g. $CaCO_3$.			0.2 g. $MgSO_4$.			0.2 g. $CaSO_4$.			0.2 g. Na_2SO_4.		
	Days.	Kind of Ppte.	Amount of Ppte.	Days.	Kind of Ppte.	Amount of Ppte.	Days.	Kind of Ppte.	Amount of Ppte.	Days.	Kind of Ppte.	Amount of Ppte.	Days.	Kind of Ppte.	Amount of Ppte.
Pyrite	8	FeS	Trace*	60	FeS	Trace*	30	Fe ox.	Incompl.				8	FeS	Trace*
	30	FeS	Complete	200	FeS	Complete	180	FeS	Complete				30	FeS	Complete
Hematite	8	FeS	Trace				30	FeS	Trace*						
	30	FeS	Complete				200	FeS	Complete						
Magnetite	10±	FeS	Trace	36	FeS	Trace	60	FeS	Trace	4	FeS	Trace*	5	FeS	Trace
	30	FeS	Complete	200	FeS	Complete	200	FeS	Complete	30	FeS	Complete	30	FeS	Complete
Siderite	14	Fe ox.	Small				40	Fe ox.	Small	14	Fe ox.	Large	30		None
	30	Fe ox.	Incompl.				180	FeS	Complete	30	Fe ox.	Incompl.	200	Fe ox.	Very small
Augite	8	Fe ox.	Small				8	White	Small						
	30	FeS	Complete				200	FeS	Complete						
Olivine	8	Fe ox.	Small				60		None						
	30	FeS	Complete				200	FeS	Complete						
Greenalite	8	Fe ox.	Small												
	30	FeS	Complete												
Glauconite	8	Fe ox.	Small	40	FeS	Trace	8	White	Small	30	Fe ox.	Incompl.	30		None
	30	FeS	Complete	200	FeS	Complete	200	Fe ox.	Very small				200	Fe ox.	Very small

* "Trace" means that precipitation is just started. "Incompl." means that precipitation of iron is incomplete. In every case FeS gave tests for Fe and S.

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were added, and half of the tubes were stoppered, the other half being left open except for cotton plugs to keep out dust. A large number of such experiments were performed, those in stoppered tubes being recorded in Table VII. In the table the smaller number under "days" indicates the time required for a precipitate to become noticeable. The second figure shows the number of days before the sample was analyzed. "FeS" means that a black precipitate, containing iron and sulphur, formed. "Fe ox." stands for a brown precipitate containing iron.

In the open tubes most solutions, on addition of salts, lost most of their iron in less than thirty days, but a few parts per million remained in solution. In some open tubes the iron was precipitated first as black sulphide, which changed to brown a little later. In those cases only was precipitation complete. Magnesium carbonate, in the presence of air, precipitated the iron incompletely in a few days (see Precipitation diagram, Fig. 45). From

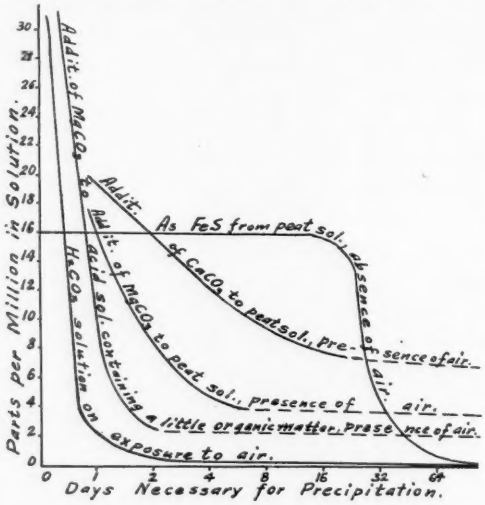

FIG. 45. Precipitation diagram showing approximate stability of iron in solutions with and without organic matter. Broken lines indicate that iron remaining in solution was probably in the colloidal state.

3 to 5 parts of iron stayed in solution for a long time. This iron will *not* pass through the collodion or parchment dialyser and, therefore, is most probably colloidal. It *cannot* be detected in the solutions except after addition of hydrochloric or some other highly ionized acid. Calcium carbonate precipitates iron from peat solutions as hydroxide more slowly, and from 4 to 8 parts of iron may stay in such solutions for many months (see Fig. 45).

When $MgCO_3$ or $CaCO_3$ was added to a solution (in a stoppered bottle) which had obtained its iron through the action of acid set free by adsorption (p. 432), iron sulphide was *never* precipitated, but iron hydroxide was precipitated incompletely (see Fig. 45). Two to five parts of iron per million stayed in solution. Since these solutions contained very little organic matter, it seems that very minute amounts of it are sufficient to hold some iron in solution. The fact that no iron sulphide formed in these solutions may be due to the presence of too little organic matter and the relatively great acidity of the solutions before the carbonate was added. It seems improbable that sulphide-producing bacteria existed in these acid solutions, for they are supposed to live in neutral or alkaline solutions.[67]

Probability of the Presence of Sulphide-producing Bacteria.— Certain bacteria[68] produce hydrogen sulphide directly from decaying organic matter. Others take oxygen away from sulphates, producing sulphides which may react with iron salts to produce iron sulphides. It is stated that organic matter reduces sulphates to sulphides directly, but this probably does not take place except at high temperature, as experiments by Allen[69] and others[70] have shown.

In the experiments recorded here, no hydrogen sulphide was

[67] See culture media cited by Harder, *op. cit.*, pp. 41–43.

[68] Harder, E. C., *op. cit.*, pp. 40–44.

[69] Allen, E. T., Crenshaw, J. L., and Johnston, J., "The Mineral Sulphides of Iron," *Am. Jour. Sci.*, 4th ser., vol. 33, 1912, p. 171.

[70] Siebenthal, C. E., "Origin of the Zinc and Lead Deposits of the Joplin Region, Missouri, Kansas, and Oklahoma," U. S. Geol. Survey, Bull. 606, 1915, p. 62.

produced or iron sulphide precipitated in any peat solution, unless some salt was added, although such solutions (Table I.), after having been filtered, stood over a year in the absence of air. Other experiments were made bearing on this point. Ferric sulphate (0. 1 gram) was added to peat solutions in sealed bottles (500 c.c.). No iron sulphide formed within 5 months. When a little solid peat was added to the solutions, no precipitate of sulphide formed. Similar results were obtained with ferrous sulphate.

If we assume that in the experiments of Table VII. chemical reactions took place without the aid of microörganisms, it is difficult to understand why many weeks should be necessary in one case and only a few days in another to produce the same result in similar solutions.

When peat solutions which had been in contact with magnetite were treated with different concentrations of the same sulphate, it was found that ½ gram of a sulphate added to 75 c.c. of solution in a stoppered test tube usually caused the precipitation of black colloidal FeS in about 15 to 30 days. One gram precipitated FeS at the beginning, but after some time the iron came down as brown hydroxide. Two grams seemed to be without any effect whatever on the iron of the solution. The writer can find no explanation for such behavior due to the concentration, except that greater concentration of sulphates may make solutions toxic for organisms. It seems, then, that microörganisms played an important part in the precipitation of the sulphide of iron.

The black sulphides, if the solutions are exposed to air, are oxidized extremely rapidly.

Experiments on Replacement of Calcite and Silica by Iron.—A number of experiments were made with peat solutions to find out, if possible, the speed of replacement of calcite and silica by iron oxide. Microscopic slides of oölitic limestone, opal, and siliceous oölite were put into bottles containing peat solutions which had been in contact with iron oxides, and contained over 20 parts of iron. The solutions were renewed once a month. All bottles were kept stoppered.

With oölitic limestone, it was found that the calcite would go into solution slowly and would be replaced by a soft dark brown mass in which the oölitic structure was still visible. On being dried in the air, the mass cracked in many places. Small recent shells of calcium carbonate were introduced in the same manner. In them only the surface was coated or replaced by the brown mass. In every case the brown mass consisted of iron and organic compounds.

In one experiment a mixture containing about 200 parts per million of iron, and made up half of peat solution and half of $N/50$ H_2SO_4, was used. The shell in this solution was completely replaced by a very soft dark brown mass which contained iron.

A small piece of soft crumbling oölitic limestone was treated like the microscopic slides. After a few months, black iron sulphide with organic matter had formed a thin coating on it. In the experiments with slides of opal and siliceous oölite, no changes could be detected, even after one year.

Protective Colloids.—The sulphates and chlorides are strong electrolytes and would be expected to precipitate the colloidal organic matter, but such precipitation occurred only to a very minor degree, even after many months of standing.

The humus colloids, therefore, seem to belong to the group called emulsoids or reversible colloids, which are coagulated only very slowly, and whose precipitation is reversible.[71] Such emulsoids have the property of exercising protective action for suspended colloids, even when present in minute amounts. That such protection is afforded by humus colloids is suggested by the fact that in the majority of experiments in which black FeS was formed as the end-product of the reaction, this sulphide appeared as colloidal suspension and was not precipitated for many days or weeks, even in the presence of electrolytes. It is also probable that the same protective action is responsible for the large amounts of silica that can be held in suspension by such humus solutions, as well as the small amounts of iron that could not be precipitated.

[71] Bancroft, W. D., *op. cit.*, p. 170.

Precipitation of Silica.

It was formerly believed that silica was carried in solution as alkaline silicate and that on separation from the alkali the silica was precipitated,[72] but it is now held that silicates are hydrolyzed and that silica is carried as colloid in dilute natural solutions.[73]

As a colloid, silica usually carries a negative charge,[74] but under certain conditions the charge is positive. According to Zsigmondy,[75] silica in solutions with less than one per cent. of SiO_2 is sometimes stable for years, and is coagulated immediately by relatively few electrolytes. Taylor[76] states that colloidal silica is positively charged in acid solutions, and negatively in alkaline or very feebly acid solutions. A definite concentration of an electrolyte is necessary for precipitation. An excess or insufficient amount of the electrolyte is usually ineffective, or causes only partial precipitation.

Dean,[77] in recent experiments, found that dialyzed silica would not be precipitated from a solution containing only $CaCO_3$, but that it would coagulate quickly if CO_2 was bubbled through to form the bicarbonate of calcium. W. A. Tarr[78] observed that silica as sodium silicate in dilute solutions was precipitated by sea water. Lovering[79] treated a dialyzed solution of silica with carbon dioxide and obtained a precipitate of silica. The writer took one of his own solutions in which $N/50$ sulphuric acid had acted

[72] Dienert, M. F., "Etude de la dissolution des elements constituant les sables alluvionnaires par les eaux souterraines," Bull. Soc. Chem., 4th ser., vol. 13, 1913, pp. 381–394.

[73] Kahlenberg, L., and Lincoln, A. T., "Solutions of Silicates of the Alkalies," *Jour. Phys. Chem.*, vol. 2, 1898, p. 90.

For other references see:

Leuher, V., and Merrill, H. B., "The Solubility of Silica," *Jour. Am. Chem. Soc.*, vol. 39, 1917, p. 2630.

[74] Zsigmondy, R., *op. cit.*, p. 211.

[75] *Op. cit.*, p. 211.

[76] Taylor, W. W., "The Chemistry of Colloids and Some Technical Applications," New York, 1915.

[77] Dean, R. S., "Formation of Missouri Cherts," *Am. Jour. Sci.*, vol. 45 1918, p. 413.

[78] Tarr, W. A., "Origin of Chert," *Am. Jour. Sci.*, vol. 44, 1917, p. 409.

[79] Unpublished thesis, Univ. of Minnesota.

on serpentine and which contained 120 parts of SiO_2 per million, and added just enough sodium carbonate to make the solution slightly alkaline. All the silica coagulated immediately. If no carbonates were added to these sulphuric acid solutions, silica was not observed to coagulate during the time of observation (nine months). If a number of these acid solutions with silica derived from various minerals were poured into one container, no silica was precipitated, though the solutions differed widely in composition. They had one point in common, however—all were acid.

It seems, then, that silica in dilute solutions is precipitated only when its charge is neutralized, or changed to the charge opposite to that which it had. It would not be likely, therefore, that an acid solution would lose its silica on meeting another slightly acid solution.

Experiments with Filtered Peat Solutions.—To a peat solution (500 c.c.) that had been in contact with greenstone and contained 68.0 parts of SiO_2 and 15.3 of Fe per million was added ½ gram of $MgCO_3$. The solution was kept out of contact with air. After one month 52.0 parts of SiO_2 and 8.1 of Fe had been precipitated. A sample of the original solution without $MgCO_3$ remained unchanged.

The same procedure was followed with a solution from olivine containing 106.0 parts of SiO_2 and 9.2 of Fe (ratio 11:1). After one month, 45.0 parts of SiO_2 and 3.4 of Fe (ratio 13:1) were still in solution.

In a similar experiment with a solution from serpentine containing 83.0 parts of SiO_2 and 4.0 of Fe (ratio 21:1), after 30 days 59.0 parts of SiO_2 and 2.5 parts of iron (ratio 24:1) remained in solution. The slowness and incompleteness of the precipitation of silica, as well as that of iron in these three experiments, is significant.

The following experiments show that silica is not precipitated by electrolytes of sea water nor some of the other common electrolytes, even if iron contained in the same solution is precipitated as sulphide.

To 1,000 c.c. of a solution of artificial sea water which had been in contact with peat and greenstone (p. 433) were added 1,000 c.c. of peat solution from olivine (Table I.). The mixed solution, which was kept in a stoppered vessel, contained 124 parts of SiO_2 and 133 of Fe per million. Within a day the solution became turbid and a black colloidal iron sulphide slowly formed. It did not coagulate entirely within forty days. After that time the solution was filtered. The precipitate contained only black FeS and organic material. After 2 more months the solution had become clear. An analysis showed that no silica whatever had been precipitated.

When 250 c.c. of peat solution from olivine (106.0 SiO_2, 9.0 Fe) were mixed with 250 c.c. of "artificial" sea water (p. 433), no precipitate was produced within several months.

In the following four experiments, the filtered solutions were from the peat solution in contact with serpentine, and contained 83.0 parts of SiO_2 and 4.0 of Fe per million.

1. 250 c.c. of solution were mixed with 250 c.c. of artificial sea water. No precipitate occurred in 4 months. For the first two months the vessel was stoppered.

2. To 400 c.c. of solution 1 c.c. of concentrated H_2SO_4 was added. After two weeks the solution still contained all its silica. Hydrochloric acid acted the same way.

3. Carbon dioxide was bubbled through the solution for 30 minutes. No precipitate formed during two weeks, the time of observation.

4. Three grams of pure white kaolinite were added to 300 c.c. of solution in a closed bottle, which was agitated a few times. After 16 days most of the iron had been precipitated. Of 83 parts of SiO_2 13.5 were still in solution.

Conclusions.

Precipitation of Iron from Organic Solutions:

1. In the presence of air, iron is precipitated exceedingly slowly, if at all.

2. The addition of sand, crushed chalcedony, or orthoclase does not accelerate precipitation noticeably.

3. The addition of carbonates of alkalies and alkaline earth metals to a solution exposed to air causes *incomplete* precipitation of iron as hydroxide. In the absence of air, similar reactions occur, but often iron sulphide is precipitated instead.

4. Sulphates of alkalies and alkaline earth metals added to a solution in the presence of air may first cause precipitation of a sulphide which changes to a hydroxide, or may precipitate the hydroxide directly. In the absence of air, the iron is precipitated by these sulphates, either as a sulphide when precipitation of iron is complete, or as hydroxide when precipitation is incomplete. When the amount of sulphate exceeds a certain limit, no precipitation as sulphide occurs.

5. At low temperature organic matter alone does not reduce ferrous or ferric salts to iron sulphide. Bacteria seem to be necessary.

6. From natural organic solutions iron is usually *not completely* precipitated as hydroxide. From 2 to 8 parts per million remain in solution (see diagram, Fig. 45).

These amounts are in agreement with those found in river waters containing organic matter. As iron, with the possible exception of a fraction of one part per million, is precipitated from surface waters unless organic matter is present, it is highly probable that larger amounts are *carried as organic colloids* or *adsorbed by organic colloids,* and *not* as *bicarbonate.*

Precipitation of Silica.—Colloidal silica in inorganic solutions and natural organic solutions behaves differently.

In inorganic solutions silica is relatively unstable and therefore easily precipitated by certain electrolytes and colloids with an opposite charge. Carbonic acid, carbonates of the alkalies, and bicarbonates of the alkaline earth metals seem to be among the most efficient precipitants. It depends on the initial charge of the colloids of silica which electrolyte will act. Silica with a positive charge is easily precipitated by an electrolyte which neutralizes the charge or gives the colloid a negative charge, provided

that the solution is of the proper concentration. The reverse also takes place.

In natural organic solutions which contain protective colloids, silica follows the same laws, but on account of the protection afforded by the organic colloids, it is precipitated much more slowly, and apparently incompletely, in some cases. Electrolytes, such as the salts of sea water, seem to be ineffective as precipitants. The formation of colloidal iron sulphide does not cause precipitation of silica.

ORIGIN OF THE BIWABIK FORMATION.

Previous Views on the Origin.[80]

H. V. Winchell[81] in 1892 concluded that the iron formation consists of chemical and mechanical oceanic deposits. N. H. Winchell[82] in 1899 accepted Spurr's[83] hypothesis that the iron formation was a glauconite-like formation, but later he[84] proposed that the greenalite resulted from a volcanic sand. Leith[85] objects to Spurr's glauconite hypothesis (see p. 417) and thinks that colloidal silica may have combined with ferrous iron to form greenalite. He concludes: ". . . that the greenalite granules may possibly have developed directly from the abstraction, through the agency of organisms of iron from solution in sea water, whence it was contributed from adjacent land areas. . . ."

Van Hise and Leith[86] in 1911 concluded that all the important Lake Superior iron-bearing formations are very similar in origin. They believe that a very large part of the iron and silica was contributed to the ocean directly, either by magmatic emanations from igneous rocks (probably poured out on the ocean floor), or

[80] For older literature see Leith, C. K., *op. cit.*, p. 31.

[81] *Op. cit.*, pp. 138–146.

[82] Winchell, N. H., "The Geology of Minnesota," Geol. Nat. Hist. Surv. Minn., Final Rept., vol. 4, 1899, p. 359.

[83] *Op. cit.*, p. 242.

[84] Winchell, N. H., "Structural and Petrographic Geology of Minnesota," Geol. Nat. Hist. Surv. Minn., Final Rept., vol. 5, 1900, pp. 990 and 997.

[85] *Op. cit.*, pp. 242, 254, and 257.

[86] Van Hise, C. R., and Leith, C. K., "The Geology of the Lake Superior Region," U. S. Geol. Survey, Mon. 52, 1911, p. 499.

by rapid decomposition of basic igneous rocks, due to their contact, while hot with sea water. Van Hise and Leith, however, think that considerable portions of the iron and silica may have been derived from the land by processes of ordinary weathering.

Wolff [87] believes that the bulk of the iron oxides in the Biwabik formation are in the same "chemical state" now as that in which they were laid down, and that greenalite was relatively unimportant as original mineral. Grout and Broderick [88] advocate the hypothesis of the deposition of the ferruginous cherts, "with more or less siderite, ferric oxide, and greenalite" in shallow water, mainly by organic agencies.

Possibility of Direct Contribution of Silica and Iron from Magma.

Association of Lavas with Chert.—Van Hise and Leith [89] based their argument, that probably the greater part of the silica and iron of the iron-bearing formations had been contributed directly from the magma or from hot lavas poured out on the ocean floor, on the frequent association of basic igneous flows with chert and jasper. Their best evidence seems to be the discovery, near Hudson Bay, of chert and jasper grading into basalts of Algonkian age. Leith [90] says that this jasper must have been deposited "under conditions differing radically" from those observed today.

In California radiolarian cherts are associated with basalts, some of which are spheroidal and ellipsoidal.[91] Geikie [92] mentions a number of occurrences of pillow lavas and interstratified cherts. Of the cherts of the Lower Silurian (Arenig group) of Scotland he says: [93]

[87] *Op. cit.*, pp. 233–235.

[88] *Op. cit.*, p. 46.

[89] *Op. cit.*, p. 499.

[90] *Op. cit.*, ECON. GEOL., vol. 5, 1910, p. 242.

[91] Ransome, F. L., "The Eruptive Rocks of Point Bonita," Bull. Dept. Geol. Univ. California, vol. 1, 1893, p. 109.

Lawson, A. C., "Sketch of the Geology of the San Francisco Peninsula," 15th Ann. Rept. U. S. Geol. Surv., 1895, p. 420.

[92] Geikie, A., "The Ancient Volcanoes of Great Britain," London, 1897, vols. 1 and 2.

[93] *Op. cit.*, vol. 1, p. 198.

It thus appears that during the volcanic activity there must have been intervals of such quiescence, and such slow, tranquil sedimentation in clear, perhaps moderately deep water, that a true radiolarian ooze gathered over the seabottom. . . . Thus the great depth of strata which elsewhere constitute the Upper Arenig and Lower and Middle Llandeilo subdivisions is here represented by only some 60 or 70 feet of radiolarian cherts.

It has recently been pointed out by Davis[94] that pillow lavas are also intrusive, and not necessarily submarine flows. Davis presents many arguments in favor of and against the direct contribution theory of silica. Dewey and Fleet[95] believe that pillow lavas are usually accompanied by radiolarian cherts, and that the silica of the cherts was derived directly from the magma.

Scrivenor,[96] on the other hand, does not think that this hypothesis is applicable to many East Indian cherts which are probably algal cherts, but lays stress on the removal of silica by tropical weathering.

Magmatic Springs or Submarine Lava Flows Possible Source of Silica.—If direct contribution of silica from the magma is assumed, the present writer favors the hypothesis of the derivation of silica from hot submarine lava flows rather than from magmatic springs, for two reasons:

1. If we assume a siliceous water with 1,000 parts of SiO_2 per million (a much more concentrated solution than those of geysers), over 524,000 cubic miles of solution would have been necessary to transport the silica of the Biwabik formation (of 10,000 square miles area and 330 feet thickness). Such a quantity would cover an area of the size of the United States to a depth of 900 feet. The magma which could furnish so much aqueous solution would probably have to be 20 to 40 times 524,000 cubic miles in volume,[97] the equivalent of a cone with an

[94] *Op. cit.*, p. 404.

[95] *Op. cit.*, p. 244.

[96] Scrivenor, J. B., "Radiolaria-bearing Rocks of the East Indies," *Geol. Mag.*, vol. 49, 1912, p. 247.

[97] Gautier's figures for the amount of combined water in granite are about 2.5 to 3.0 per cent. in "The Genesis of Thermal Waters and Their Connection with Volcanism," abstract by F. L. Ransome in ECON. GEOL., vol. 1, 1906, p. 691.

altitude equal to the radius of the earth, and a base 10,000 square miles in area.

2. On the other hand, if we imagine hot lavas poured out on the ocean floor, there must have been tremendous chemical reaction and physical disintegration. Disintegration would not contribute colloidal silica directly to the water; but diatoms (and probably other organisms), as has been shown by Murray and Irvine,[98] can abstract silica from detrital material.

The chief objection to the theory of contribution of silica to the sea by hot lavas, in the case of the Biwabik and Gunflint formations, is that contemporaneous igneous rocks have not been found within a considerable distance. Van Hise and Leith[99] noted this, and thought that the remarkable uniform character of the Biwabik and Gunflint formations was possibly due to their distance from contemporaneous igneous activity. Nevertheless, the iron-bearing formation of the Gogebic Range,[100] which was in or near the area of igneous activity, is much like that of the Biwabik. The iron-bearing formation of Hudson Bay[101] and the Belcher Islands,[102] in which basalts occur with the sediments, is also very similar to the Biwabik formation.

Contribution of Iron from Hot Springs.—The evidence seems to show that iron and silica in the ratio found in the Biwabik formation cannot be carried in any but very weak solutions. Clarke[103] cites many analyses of spring waters high in silica and others high in iron, but no water high in both. As a matter of fact, these two elements seem to be mutually exclusive except in weak solutions. In acid waters which are high in iron, aluminum seems to be equally or more abundant, but this element is only sparingly present in the iron formation. Silica is present to only a very minor degree in the more acid waters, as would be expected

[98] *Op. cit.*, p. 245.

[99] *Op. cit.*, p. 517.

[100] Hotchkiss, W. O., "Geology of the Gogebic Range and its Relation to Recent Mining Developments," *Eng. and Min. Jour.*, vol. 108, 1919, p. 501.

[101] Leith, C. K., "An Algonkian Basin in Hudson Bay," ECON. GEOL., vol. 5, 1910, p. 227.

[102] Moore, E. S., *op. cit.*

[103] *Op. cit.*, pp. 174–195.

and as has been demonstrated by many experiments.[104] It is difficult to conceive of an acid ocean or even of an acid large inland sea. The acidity would quickly be reduced by the presence of many base-forming elements in the rocks, and unless the acidity were reduced temporarily or periodically, no iron could be precipitated. Of course, we could imagine acidity around the submarine hot springs and neutralizing conditions at some distance, where deposition occurred. Even then the probable presence of much aluminum and other metals in the solutions and the small amounts of silica would probably preclude the precipitation of ferruginous chert.

Solutions charged with carbonic acid can carry iron and silica (p. 433). Iron as bicarbonate could be present in such cold solutions to the extent of 100–150 parts per million,[105] if other salts were absent. Their presence as bicarbonates necessarily would repress the solubility of iron.[106] In hot solutions bicarbonates can exist only when pressure prevents the escape of carbon dioxide. It is obvious that this gas would have been expelled as soon as the solutions reached an open, probably shallow basin. Iron would have been precipitated immediately. Even if only a part of the carbon dioxide had escaped, from either hot or cold solutions, it would have resulted in the formation of normal carbonates like those of sodium[107] and magnesium. These are alkaline toward litmus, and precipitate iron from solution. It probably would have necessitated special currents in the sea to carry these precipitates a hundred or more miles.

Assuming that a bicarbonate solution with 100 parts of iron per million (which would require 300 parts of SiO_2 to be in the ratio of iron to silica in the cherts—more silica than probably can be held in such solution except under great pressure), we find that it would take about 630,000 cubic miles of solution to

[104] Leuhner, V., and Merrill, H. B., "The Solubility of Silica," *Jour. Am. Chem. Soc.*, vol. 39, 1907, p. 2630.

[105] Smith, H. J., "On the Equilibrium in the System: 'Ferrous Carbonate, Carbon Dioxide and Water,'" *Jour. Am. Chem. Soc.*, vol. 40, 1918, pp. 879–885.

[106] Repression of solubility by a common ion.

[107] Smith, Alex., "General Chemistry for Colleges," New York, 1920, p. 462.

furnish as much iron as is assumed to be in the Biwabik formation. An area the size of the United States could be covered with this volume to a depth of over 1,000 feet. It does not appear probable that so much aqueous solution could come from a limited area.

Derivation of Iron from Hot Lavas.—Van Hise and Leith[108] heated fresh basalt to 1,200° C. and then plunged the mass into salt water. The violent reaction ensuing produced principally sodium silicate, but relatively little iron. They say that "the experiment does not seem to suggest an adequate source for the iron in this reaction." Igneous rocks in hot or cold water react alkaline,[109] for potassium and sodium silicates (water-glass) are strongly alkaline. Therefore, it seems improbable that much iron will go into solution when hot lavas come into contact with sea water, even if some hydrochloric acid should be formed in the reaction of hot lava with sea water. A little iron may have been in the colloidal state, or adsorbed by the colloidal silica formed in such a reaction. It is probable that colloidal or adsorbed iron gives to jasper the red or brown color, but this coloring, if due to colloids, could also be formed in other ways.

Attention is called by Van Hise and Leith[110] to the association of basalts and iron-stone in Great Britain. These clay-iron-stone ores are usually associated with coal beds or vegetable remains.[111] Some of them show that molluscan life flourished on the spot at the time of formation. Geologists generally have not hesitated to connect the origin of these iron ores with the decomposition of rocks by weathering. It is probable, however, that porous, fresh basalts and tuffs on land furnished a considerable portion of the iron by their rapid decomposition, especially in the presence of abundant plant life. Chert does not occur to any extent with clay-iron-stone and associated basalt.

[108] *Op. cit.*, p. 516.

[109] Clarke, F. W., *op. cit.*, p. 475.
Cushman, A. S., "The Effect of Water on Rock Powders," U. S. Dept. Agr., Bur. Chemistry, Bull. 92, 1905, p. 9.

[110] *Op. cit.*, pp. 508–509.

[111] Geikie, A., *op. cit.*, vol. 2, p. 204; vol. 1, p. 181.

Combination of Iron with Silica.—A greenalite-like substance has been produced in the laboratory by Van Hise and Leith.[112] They state that silicic acid and a ferrous salt in the absence of air produce no precipitate, but that "ferrous sulphate reacts directly with solutions of silicates of the alkalies," forming a precipitate of silicate similar to greenalite.

In dilute solutions silica probably does not exist as alkali silicate, but as colloidal silica.[113] Therefore it should not react with ferrous salts in the absence of air to form a ferrous silicate. Soluble magnesium salts, which are plentiful in the ocean, should also be expected to form insoluble silicates with alkali silicates if iron salts did.[114] Yet only 3 to 5 per cent. of magnesia are combined with the greenalite. It is probable, therefore, that in dilute solutions the reactions are more complicated than those of simple double decomposition, possibly similar to adsorption.

Weathering Suggested as the Source of Iron.

Warm and Humid Climate Necessary.—Under certain conditions, on weathering of igneous rocks, iron oxides remain in place as some of the most stable residual constituents. Under other conditions part of the iron is carried away, though this removal may not keep pace with the abstraction of the more soluble constituents of the rocks.[115] Van Hise[116] gives a table on rock decomposition in which the loss of Fe_2O_3 compared with Al_2O_3 as zero varies between 8.78 per cent. and 88.84 per cent. In humid regions the loss of iron is much greater than in arid ones.

In tropical countries decomposition of rocks is extremely rapid and extends to great depth, sometimes as deep as 200 to 300

[112] *Op. cit.*, p. 521.

[113] Kahlenberg, L., and Lincoln, A. T., *op. cit.*, p. 89.

[114] Van Hise and Leith, *op. cit.*, p. 521.

[115] Merrill, G. P., "Rocks, Rock-weathering and Soils," New York, 1913, pp. 197–211.

Leith, C. K., and Mead, W. F., "Metamorphic Geology," New York, 1915, pp. 1–24.

[116] Van Hise, C. R., "A Treatise on Metamorphism," U. S. Geol. Surv. Monograph, 1904, p. 515.

feet.[117] Branner[118] states that in the forest-covered portions of Brazil decay is greater than in the parts devoid of dense vegetation. Decomposition, however, is not limited to any particular region. Organic acids are important factors in the decomposition, according to Branner. Under such circumstances, iron is either carried away or is accumulated as laterite deposits. In many places the laterites probably represent only a small part of the iron from the decomposed rocks. Many analyses show that, under the same conditions of laterization, titanium oxide and alumina are much more stable than iron oxide. These conditions have been described as follows:[119]

1. Alternating wet and dry seasons.
2. Tropical heat with concomitant abundant vegetation.

As to the importance of abundant vegetation there has been some disagreement. Holmes[120] states that organic growth is usually absent where lateritic deposits occur, and implies that organic matter may be unfavorable to their formation. Campbell,[121] who probably expresses the opinion of the majority of the investigators, however, thinks that sterility of the soil is caused by the formation of a hard crust of iron oxide at the surface. This oxide is deposited there during the dry seasons when iron-bearing solutions are drawn to the surface by capillarity. Changes in water table are also a factor. Simpson[122] also is of this opinion and remarks that "Primary laterite is a true efflorescence" brought to the surface by capillarity.

[117] Derby, O. A., "Note on the Decay of Rocks in Brazil," *Am. Jour. Sci.*, vol. 27, 1884, p. 138.

[118] Branner, J. C., "Decomposition of Rocks in Brazil," *Bull. Geol. Soc. Am.*, vol. 7, 1896, pp. 255–314.

[119] Maclaren, M., "On the Origin of Certain Laterites," *Geol. Mag.*, vol. 43, 1906, pp. 536–547.

Simpson, E. S., "Notes on Laterite in Western Australia," *Geol. Mag.*, vol. 49, 1912, p. 402.

[120] Holmes, A., "The Lateritic Deposits of Mozambique," *Geol. Mag.*, vol. 51, 1914, pp. 532–533.

[121] Campbell, J. M., "Laterite, its Origin, Structure and Minerals," *Mining Mag.*, vol. 17, 1917, p. 178.

[122] *Op. cit.*, p. 400.

It seems to the present writer, then, that no hard iron oxide crust could form near the surface, if really dry seasons do not exist. This seems to be borne out by the fact that areas which are relatively small, compared with the great basins of many tropical rivers, are only covered by lateritic deposits. Most of the iron must, therefore, be removed in some form or other by the surface and ground-waters, probably with the aid of organic solutions.

Iron and Silica Carried by Waters Rich in Organic Matter.

Attention was called to the large amount of silica and iron carried by rivers rich in organic matter (p. 421). The following analyses of the waters of the Amazon River and its tributaries have been taken from Katzer[123] and recalculated to parts per million:

TABLE VIII.

ANALYSES OF WATER FROM AMAZON RIVER AND TRIBUTARIES.
(Parts per Million.)

	Amazon.[124]	Amazon.[125]	Paraná-mirim.	Mæcuru.	Xingu.	Tapajos.	Itapacurá-mirim.
SiO_2	9.4	12.2	8.8	19.2	9.6	9.2	9.0
$Al_2O_3 + Fe_2O_3$	3.6	6.2	9.5	6.6	3.9	2.8	6.8
Organic matter	5.7	8.9	6.3	5.8	11.8	12.2	11.6
Total solids at 110°	39.0	54.5	59.7	52.6	57.2	50.5	64.1
Suspended organic matter	37.2	61.4	100.8	96.7	56.3	62.8	103.2
Suspended inorganic matter	63.2	135.2	111.2	99.6	31.2	28.4	188.4

Figures for CaO, MgO, K_2O, and Na_2O have been omitted. Lime is the only constituent which is abundant besides silica and iron. Al_2O_3 and Fe_2O_3 were not separated in the analyses, but there is little doubt that most of the "$Al_2O_3 + Fe_2O_3$" is iron oxide. This appears very probable when these analyses are

[123] Katzer, F., "Grundzüge der Geologie des unteren Amazonasgebietes," Leipzig, 1903, p. 45.

[124] Amazon River at Obidos at a depth of 26 m.

[125] Amazon River at Obidos at a depth of 0.5 m.

compared with those of other South American and tropical streams in which iron is almost always greatly in excess over aluminum. These analyses seem to be in accord with experimental evidence of the writer (p. 445), in which it was shown that iron up to 8.5 parts per million was exceedingly stable in organic solutions. A similar agreement is found between the amount of silica held by the tropical rivers, and that contained in the organic peat solutions of the laboratory.

According to Katzer,[126] the Amazon River normally has a flow of 120,000 cubic meters per second, 200 miles from its mouth. During flood time this volume may increase several fold. If an average of three parts of iron per million is assumed for the water (which would be in keeping with the analyses), the Amazon River in 176,000 years could carry 1,940,000 million metric tons of iron to the sea—the amount assumed for the Biwabik formation (p. 413). The amount of silica carried would be correspondingly large.

In a basin the size of that of the Amazon River, the iron from rock of a thickness of only a few feet would be needed to furnish the stated amount. We may postulate conditions assumed by others[127]—many fresh basalt flows and tuffs on land, possibly with much pyrite like that in the greenstone of the Lake Superior region. Under such conditions enough iron could be dissolved from a much smaller area than the Amazon Basin without there being decomposition to a greater depth than is common.

The following additional reasons favor the hypothesis that iron and silica were derived from land and transported by rivers rich in organic matter:

1. A steady supply of material over a long period would be assured by such a source.

2. No abnormally acid or basic solutions would have been necessary to carry the salts of iron and silica to their places of deposition without suffering premature precipitation.

3. Carbon dioxide, derived from the oxidation of organic mat-

[126] *Op. cit.*, p. 38.

[127] Van Hise and Leith, *op. cit.*, pp. 512 and 514.

ter on the sea floor, could prevent the deposition of calcium and magnesium carbonate to a certain extent by the formation of soluble bicarbonates.

4. The average sedimentary rock contains less magnesia and more lime than the igneous rock from which it is derived.[128] The Biwabik formation contains more magnesia than lime. Experiments dealing with adsorption by organic and inorganic matter seem to show that magnesia is adsorbed more rapidly than and probably in preference to lime. Moreover, the great abundance of ferromagnesian minerals, whether igneous or metamorphic, suggests a closer relationship between iron and magnesium than between iron and calcium.

5. If we consider rivers rich in organic matter as the transporting agency, it does not seem necessary to account for anything except the lack of lime in the iron formation. There is no reason why calcium and the larger part of magnesium carried to the sea by such rivers could not have been deposited in a different, probably a deeper, part of the ocean. The occurrence of almost pure limestone certainly proves that there has been separation of the constituents of river waters. Moreover, there exists a gradation between iron-bearing formation and carbonate rocks on the Gunflint Range and the east end of the Gogebic Range.[129]

6. The Biwabik and Gunflint formations show no signs of volcanic disturbance, either sudden uplift or sinking of the sea floor during sedimentation. A slow steady subsidence probably took place. If great volcanic activity had occurred within a hundred miles, some indications might be expected in the structure of the sediments.

7. Lavas were extruded during Keewatin time in greater quantities than during any succeeding period, yet the greatest development of iron-bearing formations occurred during the Upper Huronian. This suggests, at least, that these lavas were the source of iron-bearing sediments not so much during the time of their extrusion, as during their exposure to weathering much later.

[128] Leith and Mead, *op. cit.*, p. 84.
[129] Van Hise and Leith, *op. cit.*, p. 515.

8. There exist large iron-bearing formations which are not associated with larger masses of contemporaneous basic igneous rocks. The pre-Cambrian (?) Itabira formation of Minas Geraes, Brazil, is such a primary sediment.[130] Harder and Chamberlin express the opinion that bacteria may have caused the precipitation of the iron oxide in it.

Organic and Chemical Precipitation.

The existence of iron bacteria and algæ at the time of deposition of and in the Biwabik formation makes organic precipitation highly probable. Drew[131] has shown the importance of bacilli in organic precipitation of limestone. Algæ, radiolaria, and diatoms cause the deposition of silica.[132] Iron bacteria, as shown by Harder, are some of the most efficient precipitating agents of iron. According to him[133] and to Ellis,[134] all traces of iron bacteria may easily become altered beyond recognition. Mumford[135] believes that a certain type of bacillus can precipitate iron under anaerobic conditions, when some of the precipitate will become partially reduced to the ferrous state (not sulphide). If this is the case, it might offer an explanation for the occurrence of a part of the ferrous iron. Though iron bacteria of the higher type have not been found in sea water, this does not preclude their existence there. Neither are we sure that the Biwabik formation was deposited in sea water.

Bacterial action, however, does not mean that inorganic processes did not take part in the precipitation of iron and silica. Temporary conditions may be imagined under which algæ and

[130] Leith, C. K., and Harder, E. C., "The Hematite Ores of Brazil and a Comparison with the Hematite Ores of Lake Superior," Econ. Geol., vol. 6, 1911, p. 670.

Harder, E. C., and Chamberlin, R. T., "The Geology of Central Missas Geraes, Brazil," *Jour. Geol.*, vol. 23, 1915, p. 403.

[131] *Op. cit.*

[132] Murray, J., and Irvine, R., *op. cit.*, p. 245.

[133] *Op. cit.*, p. 80.

[134] Ellis, D., "Iron Bacteria," London, 1919, p. 169.

[135] Mumford, E. M., "A New Iron Bacterium," *Chem. Soc. Jour.*, vol. 103, 1913, p. 650.

bacteria could not thrive. For example, it is probable that certain algæ become extinct with the disappearance of clear water, as is indicated by the vanishing of the algal structures in the Upper Cherty division west of Hibbing, where they enter horizons with abundant slate layers interstratified with the cherts.

Special conditions are required for the separation of mechanical sediments from chemically dissolved or colloidal matter. This separation must depend on physiographic conditions similar to those for the formation of glauconite of which Murray and Renard[136] say that it is found "most characteristically on the continental slopes of high and bold coasts where currents from different sources alternate with the season."

Alterations of Original Sediments.

Grout and Broderick[137] have emphasized certain changes of oxidation and re-solution which probably took place during deposition. The writer observed similar phenomena. In Fig. 46

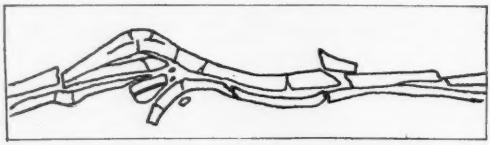

FIG. 46. Sketch showing deformation and breaking of a dense slate-like layer. Natural size.

one is illustrated. A hard slaty layer has buckled and broken in several places. Such breaking may have given rise to intraformational conglomerate. Fig. 42 seems to prove that solution went on at the surface of carbonate precipitates, producing the stylolitic surface upon which slate was laid down. Probably most of the organic matter in the precipitates, while still at or near the surface, was oxidized to carbon dioxide. This could have caused local re-solution of iron which was then re-deposited under different conditions. Such a process may have led to the formation of irregular bands of iron oxides and carbonate (page 411), which do not

[136] *Op. cit.*, p. 234.
[137] *Op. cit.*, Bull. 17, p. 42.

seem at all related to original sedimentation. Many other reactions probably occurred at that time.

Amphiboles and magnetite were formed, on deep burial of the formation. The ferruginous cherts are the result of this metamorphism.[138]

CONCLUSIONS.

From the foregoing discussions, the following conclusions may be reached: During Upper Huronian time there existed large land areas in North America which were covered largely with greenstone and basalts. It is probable that fresh extrusive rocks and volcanic tuff and ash were deposited on parts of the land, as well as in the sea basins then existing. The climate of the continent was humid and probably tropical or sub-tropical. Vegetation of a low form was abundant, and aided in the rapid decay of the rocks. Under these conditions iron, which usually is one of the most stable elements in weathering, went into solution to a large extent, but only in waters with organic colloids was it stable for any length of time in the zone of oxidation. Silica was also dissolved on a large scale. Both iron and silica were carried to the sea by rivers rich in organic matter.

Whether this was a large inland sea or the ocean is a matter of speculation. There is little to indicate that the iron-bearing cherts could not have been precipitated in fresh water. The suspended material carried by the rivers was deposited probably in deltas, while the stable colloids of iron and silica were carried by currents to places of shallow and clear water. Only under exceptional conditions did mechanically suspended material reach these places and become deposited as slate. Such exceptional conditions may have been unusually large floods, and temporary changes in the coast lines.

The precipitation of silica, iron, and part of the organic colloids was caused chiefly by algæ and bacteria, which used the organic matter for their life processes and the inorganic silica or iron for the building of their cells or sheaths. It is also probable that inorganic reactions caused much colloidal silica, iron, and

[138] Gruner, J. W., *op. cit.*, p. 13.

organic matter to be precipitated. By adsorption some of these colloids partly united to form indefinite amorphous iron silicates. These may have been ferrous silicates from the beginning, or may have been ferric at first. Iron hydroxides and silica probably did not form silicates at many places. One reason may have been that the iron was not of the proper valence or condition to make a silicate.

A large part of the colloidal precipitates assumed the shapes of oölites, differing, however, from typical ones in their internal structure. In many places the granules thus formed seem to be made up of groups of cells; this suggests algæ or similar plants. It is thought improbable that all of the granules showing oölitic shape were deposited originally as ferrous silicate. A large portion of them probably consisted of iron oxides, cherts, or carbonates.

A part of the silica contained in the taconite may have been contributed to the sea directly by magnetic springs or hot submarine lava flows. We do not believe, however, that much iron had this origin.

Before a freshly precipitated layer of iron-bearing formation could be buried to any depth, there was considerable alteration of the amorphous material. Re-solution and diffusion in one place and redeposition in another were accompanied by reduction and oxidation of portions of the iron. Most of the organic matter was oxidized to carbon dioxide at this time. On deeper burial, ferruginous chert (taconite) originated by the formation of magnetite, amphiboles, and coarse-grained carbonates from the amorphous minerals and substances. During later elevation above the sea, some of the ferruginous chert was changed to ore under favorable conditions of weathering.

UNIVERSITY OF MINNESOTA,
MINNEAPOLIS, MINN.

EXPERIMENTAL STUDY OF THE INVASION OF OIL INTO A WATER-WET SAND.[1]

ORREN W. SKIRVIN.

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INTRODUCTION.

Since the successful prediction of commercial deposits of petroleum in porous strata depends to a large extent on a knowledge of the several factors which influence and control its segregation and accumulation in such strata, it seems profitable to devote some time to the study of those factors which are known or at least thought to exert such an influence. The purpose of this paper is to present in a preliminary way the results of a number of experiments which were arranged and performed with the object of determining what relations exist between the physical properties manifested by crude oil, water, and sand, in contact—and the process of accumulation of oil in sands of various textures and porosities.

ACKNOWLEDGMENTS.

A number of published works on soils were consulted in the hope of finding definite information concerning the behavior of liquids in porous soil at and near the surface. The following books were found of especial interest and deserve mention: "Phys-

[1] Presented before the Society of Economic Geologists, Amherst Meeting, Dec. 29, 1921. Introduced by Roswell H. Johnson.

ical Properties of the Soil"—Robert Warington; "The Soil"—Sir A. D. Hall; "Soils"—E. W. Hilgard.

The writer is also greatly indebted to Roswell H. Johnson, professor of oil and gas production, and to Dr. Gebhard Stegeman, assistant professor of physical chemistry at the University of Pittsburgh, for valuable suggestions during experimental investigations and for the use of apparatus in the determination of porosity, surface tension and viscosity.

APPARATUS AND CONDITIONS OF EXPERIMENTATION.

The apparatus used for the experiments consisted of a glass percolator, slightly cone-shaped, with top and bottom diameters of 4.6 inches (11.7 cm.) and 2.9 inches (7.4 cm.) respectively and a height of 7.4 inches (18.8 cm.). A second percolator of similar dimensions was used in connection with rubber tubing as a container from which to introduce the invading liquid into the sands previously arranged as desired in the original percolator.

A dividing sheet of thin cardboard was cut to fit the percolator on a diameter and with this in place the interior of the percolator was divided into two compartments into which different grades of dry sands could be poured without intermixing. The cardboard was then withdrawn leaving the different sands arranged vertically in place with a definite line of contact between them.

The experiments were all carried out at room temperature and with a pressure on the liquid in the sand of approximately a 1.4 foot head of water.

MATERIALS USED.

The physical properties of the sands and liquids used for experimentation are recorded in Tables I., II. and III. on the following page. The sands are designated by small letters, and the oils by numbers. The only quality of water used was that which is shown in Table III.—a sodium chloride brine having a specific gravity of 1.100. The sands used were white quartz beach sands.

EXPERIMENTS.

The first group of experiments was performed to show the effect of invasion of oil-saturated sands or strata by water. The dry sands were arranged with a sand of medium-sized grains (*c*—Table I.) on top and bottom and sands of relatively coarse and fine grains arranged vertically near the center.

After the sands were completely saturated with oil a connection was made with a container of water (chloride brine—Table III.), invasion of the oil-saturated sands being induced by elevating the container.

Various combinations of sands were used together with the three grades of oil shown in Table II. In each case the invading water entered the relatively coarser-grained sand more easily than the relatively finer-grained sand regardless of the porosities of the two sands.

When the difference in grain sizes of the two sands at the center of the percolator was relatively large (as sands *a* and *d*, *b* and *e*, *c* and *f*—Table I.) the oil retained in the finer of the sands remained there indefinitely, that is, there was no dispersion after the invading action ceased. If, however, the difference in sizes of grains was comparatively small (as sands *b* and *c*, *d* and *e* —Table I.) the oil in the finer sand either moved out with the

TABLE I.

SANDS USED FOR EXPERIMENTATION.

Sand Designation Mark.	Diameters of Grains in Millimeters.		Total Porosity Percentage of Volume of Sand.
	Maximum.	Minimum.	
a.....	0.833	0.589	38
b.....	0.589	0.295	37
c.....	0.295	0.147	38
d.....	0.147	0.104	39
e.....	0.104	0.074	40
f.....	0.074	....	37

TABLE II

OILS USED FOR EXPERIMENTATION.

Oil Designation Mark.	Source of Oil.	Color.	Gravity 60° F. (15.6° C.).		Viscosity "Saybolt" at 100° F. (37.8° C.).	Viscosity "Engler" at 100° F. (37.8° C.).	Surface Tension Dynes per Cm. at 86° F. (30° C.).
			Specific.	Baumé.			
1.....	Pennsylvania...	Black	0.8178	41.2	40.4	1.33	25.32
2.....	Oklahoma.....	Black	0.8745	30.1	95.2	2.67	25.45
3.....	Texas.....	Black	0.9265	21.1	2863.0	76.44	26.96

TABLE III

WATER USED FOR EXPERIMENTATION.

Liquid.	Specific Gravity at 60° F. (15.6° C.).	Viscosity Coefficient in C.G.S. Units 68° F. (20° C.).	Surface Tension Dynes per Cm. at 86° F. (30° C.).
Water + NaCl.....	1.100	0.0100	74.9

oil from the coarser sand—but at a slower rate—or was displaced soon after the oil had been removed from the coarser sand. In such cases the finer grained of the two sands always retained more oil by adhesion, that is, the displacement was not as complete in the finer sand as in the coarser.

When an oil of high viscosity (Oil 3—Table II.) was used the adhesion to the sand grains was so great that the slight pressure available with the type of apparatus used was not sufficient to effect anything like complete displacement from even a relatively coarse sand. The experiments of this group with this oil may be regarded as unsuccessful except in so far as they tend to show the effect of adhesion on movements of viscous oils.

The second group of experiments shows the effect of invasion of water-saturated sands by oil. The sands were arranged as in the previous experiments and saturated with water (chloride brine—Table III.).

After complete saturation with water a connection was made with a container of oil and invasion induced by elevating the container. In each case the oil entered the coarser of the two sands leaving the finer sand saturated with water—regardless of the relative porosities of the two sands. When heavy oils of high viscosity were used (Oil 3—Table II.) the same results were obtained although the time factor was very much larger than for a light oil of low viscosity (Oil 1—Table II.).

In studying the effects of surface tension on accumulation some secondary experiments were performed with capillary tubes and with small glass tubing filled with sand. The inner walls of a capillary tube are wet with a thin film of oil by passing oil through the bore and then draining for thirty or forty minutes. If now one end is immersed in a beaker of water there will be no rise above the level of the water outside. On the contrary if a capillary tube is first wet with water and then immersed in oil the rise of oil within is practically normal. To demonstrate this effect in a sandstone reservoir a glass tube was filled with a slightly oil-wet sand and one end of it held in water. There was no rise of the water within whereas the dry sand in a tube acts as a very good capillary or rather series of capillaries.

CONCLUSIONS.

It has been shown experimentally that water invading an oil-saturated sand body containing a relatively coarse-grained and a relatively fine-grained sand will (within certain limits) displace the oil from the coarse sand and not from the fine sand. It has also been demonstrated that oil invading a similar sand body, but water-saturated, will displace the water from the coarse sand and not from the fine sand. There is no dispersion after the experiment in the latter case, nor in either case if the difference in grain size of the two sands—and therefore the difference in size of pores—is greater than a certain limiting value which has not been determined.

From these considerations it would appear that whether oil is

found in coarser- or finer-grained sands or strata than the adjacent strata—assuming the rocks to be water "wet"—depends on whether the oil has accumulated by displacing water or whether the oil is the residual fraction retained in the finer-grained portion of the reservoir after the displacement or removal of that in the more open portion by invading water. Commercial deposits of oil usually occur in the more open portions of a water "wet" sand, that is, in those portions of a reservoir in which the pore spaces are larger than the surrounding ones, provided there are irregularities in the sand body. We would infer, then, that such deposits are the result of oil displacing water from a more open part of a sand body. That this view is in accord with the anticlinal theory and its hydraulic modifications is attested by the carefully performed experiments of Mills[2] in which oil was made to displace water from the relatively coarse tops of domes and their analogies—but not from the fine-grained "cap" sands above, by the action of relatively weak hydraulic currents.

The relative viscosities of oil and water, oil, especially the heavier grades, being more viscous, tend to effect a segregation of oil in the larger pores whenever the motion of the two liquids is from larger to smaller pores. This is true because the resistance of small pores to viscous oil is much greater than that offered by the larger pores, while at the same time the resistance of small pores to water is much less than their resistance to the more viscous oil.

Adhesion of oil to a sand particle is a function of the attraction of the molecules of the substance composing the grain for the molecules of oil. When this attraction is greater than the internal molecular attraction of the liquid, the substance is wet by the oil and adhesion becomes greater in proportion to the magnitude of excess attraction. Since all mineral oils wet the sand or reservoir material we have assumed that the attraction between the molecules of the two substances at their surface of separation is

[2] Mills, R. A., "Experimental Studies of Subsurface Relationships in Oil and Gas Fields," Economic Geology, vol. XV., no. 5, pp. 398–421, 1920.

greater than the molecular attraction within the oil. The rôle of adhesion is to retain as much oil as possible in contact with the sand surfaces. When adhesion is relatively small, as with most light oils of low viscosity, the actual amount which a sand surface is able to retain when the liquid is subjected to a displacement force is small compared to the amount retained under similar conditions when the adhesion is great. Since viscosity is the result of internal molecular attraction or friction, while adhesion is the attraction or friction at the surface of contact with sand particles, it is seen that both work toward the same end to oppose any force which tends to remove the oil from contact with itself or with sand grains. This is why water flooding methods for recovery of oil are much less effective with moderately viscous oils than with the light so-called non-viscous varieties. For since adhesion becomes more pronounced with higher viscosity we have both factors assuming important magnitudes as we pass from less viscous to more viscous oils.

Before discussing the effect of the difference in surface tension between oil and water on the accumulation of oil it is well to lay stress on a point recently brought out by Johnson.[3] A great many writers in dealing with capillarity have apparently assumed that the surface tension of water to gas and oil to gas is a measure of the surface tension between water and oil. This is undoubtedly an error, for it can be shown mathematically that the upper limiting value of the surface tension between oil and water is less than 46 dynes per centimeter, while the lower limiting value is zero. The capillary tube experiments previously described seem to indicate that the surface tension between water and an oily surface is zero, or at least very slight, for there was no rise of water within the tube when the walls were wet with only a thin film of oil. The contact in this case is necessarily a water-oil one, because the oil from the bore of the tube spreads out over the surface of the water within, eliminating entirely the water-gas contact.

[3] Johnson, Roswell H., "The Time Factor in the Accumulation of Oil and Gas," *Bulletin A. A. P. G.*, vol. 5, no. 4, pp. 475–481, 1921.

On the contrary in the water-wet tube immersed in oil there is an oil-gas contact always present—since water does not spread out forming a film on oil—and the rise of oil within is normal, as previously noted.

In the first group of experiments conducted with oil-saturated sands with water as the invader, we should have expected, if surface tension or capillary attraction were a controlling factor, to find water displacing oil from the fine-grained sands more easily than from the coarser sands. The reason why this is not the case becomes more intelligible after a consideration of the foregoing capillary tube experiments—for it is evident that the pores of the finer sand being wet with oil have no more capillary attraction for water than have the larger pores of the coarser sand. It follows then that relative viscosity and adhesion are the important factors in such cases for the small pores offer much more resistance to movements of liquid than do the larger ones—the resistance offered by any one uniform series of openings being proportional to the viscosity and adhesion of the liquid passing through them.

If the smaller oil-wet pores of a partially exhausted oil sand offered more capillary attraction for water than the larger oil-wet pores, water flooding methods would be very much more effective than they have proved to be—for we would have simply to introduce water into the pay sand and allow it to exchange places with the oil in the finer portions of the reservoir by differential capillary attraction. This action evidently does not take place.

The theory has been brought forward by McCoy[4] that the accumulation of oil, especially the migration of oil from fine bituminous shales to adjacent reservoir rocks, is effected mainly by capillary forces. With this view the writer cannot agree because experimental evidence seems to emphasize that any series of openings of capillary dimensions wet with only the thinnest film of oil have no preferential attraction for water. Since clays and

[4] McCoy, A. W., "Notes on Principles of Oil Accumulation," *Journal of Geology*, vol. 27, pp. 252–262, 1919.

shales are more compressible than sandstones, it is mainly through pressure and the resulting reduction in volume of pore space of the bituminous shales that oil is forced out of them and into the adjacent reservoir rocks.

SUMMARY.

An experimental study of the theory of invasion was undertaken which shows that the larger pores contain the invading fluid whether this is oil that invades a water-wet sand or water that invades an oil-wet sand. This reduces the supposed rôle of differential capillarity in the distribution of oil and water in rocks, as related to their porosity. The results of a few additional experiments with capillary tubes are also discussed.

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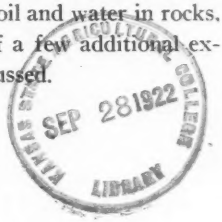


NOTES ON THE GEOLOGY OF THE BROKEN HILL DISTRICT.

E. C. Andrews.

INTRODUCTION.

Eighty years ago Broken Hill was unknown to white men, whereas today the story of its growth is a romance—not only of Australian history, but of the whole of mining endeavor.

Sir Charles Sturt, Surveyor General of South Australia, made an attempt in 1844–1846 to reach the center of the Australian Continent.[1]

The story of Sturt's strivings and sufferings in his search for the continental center, a search which led him across the site of Broken Hill township itself, furnishes one of the finest epics dealing with geographical exploration. Sturt's own simple narrative—in common with the itineraries of Eyre and of McDouall Stuart—runs as a golden thread throughout Australian history. So ignorant were the explorers as to the true nature of the inner portions of the continent that Sturt carried a large boat wherewith to explore the Central Sea. He found, indeed, great waves, but they were waves of sand in the desert instead of waves that might carry him on to success in an inland sea.

He almost perished from scurvy on the return from Broken Hill itself.

"The mean thermometer," says Sturt, "for the months of December, January, and February (1845) had been 101°, 104°, and 101°, respectively, in the shade. Under its effects every screw in our boxes had been drawn, and the horn handles of our instruments, as well as our combs, were split into fine laminæ. The lead dropped out of our pencils; our signal rockets were entirely spoilt; our hair, as well as the wool on our sheep, ceased to grow, and our nails had become brittle as glass" (p. 305).

[1] "Narrative of an Expedition into Central Australia, 1844–1846." Two vols. London, 1849.

Speaking of the privations of the return over sand hills which run for hundreds of miles in parallel crests and intervening troughs, and in which there was no sign of water, Sturt says:

"Our poor horses were not in a condition to endure much fatigue. Mr. Browne's sufferings were such that I hesitated subjecting him to exertions . . . by which I felt assured he would be ultimately overcome. . . . I dreaded every day that he might be laid prostrate as Mr. Poole[2] had been, and that he would ultimately sink as his unfortunate companion had done.

"Had other considerations, therefore, not influenced me, I could not make up my mind to persevere and see my only remaining companion perish at my side . . . under the most trying—I had almost said appalling—circumstances."

Sturt himself almost perished from scurvy on the return from Broken Hill. With failing strength, he called to him his most trusted servant, an ex-life convict, and bequeathed to him a large specimen of copper ore which he had found, and asked him, the servant—Davenport by name—not to part with this specimen at all costs, even that of his life, because it was to be presented to Queen Victoria, and would let the world know of the possible wealth of mineral in the district. Davenport not only protected the cherished specimen for the Queen, but helped most materially in bringing Sturt back to civilization.

In September, 1883, Rasp, a boundary rider of Mount Gipps Station, mistook the great Broken Hill outcrop for a tin lode, and as a result seven blocks of approximately forty acres each were taken up along the apex or line of lode.

Difficulties apparently insurmountable appeared one after the other to daunt the prospector and engineers, alike with the explorers, but step by step the great Broken Hill problem has been solved and the great city maintains itself in comfort in the center of the desert.

The now famous mining camp of Broken Hill is situated within the state of New South Wales in latitude 31° 57′ south and longitude 141° 28′ east (see Fig. 47). The main communication with the outer world is by rail to Adelaide, the capital of

[2] Poole died of scurvy and was buried at the famous Rocky Glen.

South Australia, 333 miles to the south, connecting with the main Trans-Continental Railway by way of Port Augusta. From Sydney, there are two lines of access, one 1,400 miles by rail

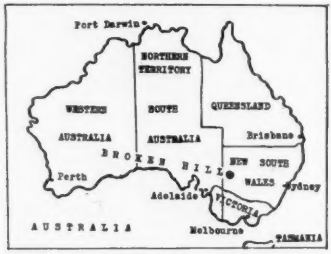


FIG. 47. Index map of Australia.

through Melbourne and Adelaide, another 750 miles by way of Cobar. Direct railway communication is established with Adelaide, thence to Sydney.

The principal minerals mined are galena and zincblende. The total estimated yield from the district is £112,000,000 ($544,320,000)[3] approximately. The value of the dividends distributed exceeds £26,000,000 ($126,360,000). One continuous ore deposit has produced this great wealth.

The lode outcrop is three miles in length. The amount of ore raised from this deposit exceeds 32,000,000 tons; the estimated ore reserves are 13,000,000 tons, and the ore which may be expected in addition to this is estimated at 7,000,000 tons.

The average rainfall for the district, taken for a period of forty years, is 9.70 inches. The maximum and minimum shade temperatures recorded are 116° and 28.5° respectively.

LITERATURE.

The main contributions to the geological literature of Broken Hill have been by C. Sturt (explorer); C. S. Wilkinson (the first Government Geologist of New South Wales), C. W. Marsh, E. F. Pittman (the second Government Geologist of New South

[3] On the basis of par exchange.

Wales), J. B. Jaquet, G. Smith, J. C. Moulden, Professor R. Beck, J. W. Gregory, the Geological Sub-Committee of the late Scientific Society of Broken Hill, Sir Douglas Mawson, and Dr. E. S. Moore.

Sturt named the district of Broken Hill the "Barrier Ranges," and recognized the schists and ironstone deposits. The lead and zinc, however, he missed, because of their failure to outcrop except as siliceous gossans containing iron and manganese.

E. F. Pittman[4] considered the Broken Hill lode to be a true "saddle."

Jaquet[5] described, in the most clear and convincing manner, the region of the oxidized zone, and Jaquet and Smith,[6] in separate papers, appear to have prophesied the importance of secondary sulphide enrichment.

Beck[7] drew attention to the peculiarities in the so-called "saddles." He seemed to suspect that minerals such as rhodonite, garnet, and feldspar were not characteristic of typical saddles.

Gregory[8] considered the Broken Hill lode to be related to a fault plane and not to be a typical saddle.

Andrews[9] (1908) noted that the hanging wall bodies were all connected directly with the footwall lode, appearing to spring therefrom. He noted also the dragging of the hanging wall against the footwall, and supplied evidence for considering the deposits to be replacements and not filling of open spaces. Jaquet,[10] however, had already stated:

"It is extremely likely that the original fissure preceding the Broken Hill Lode, which had a mechanical origin, was afterwards considerably

[4] Ann. Rept. Dept. Mines and Agric., N. S. W., 1892, pp. 108–109.

[5] "Geology of the Broken Hill Lode," Geol. Survey N. S. W., 1894.

[6] "Deposits of the Broken Hill Consols Mine, Broken Hill, N. S. W.," *Transactions Am. Inst. Min. Engineers*, vol. 26, 1897, p. 69.

[7] "Contributions to our Knowledge of Broken Hill," Records Geol. Surv. N. S. W., vol. VII., 1900, p. 20.

[8] "Broken Hill Mining—a Saddle Reef Theory," Medbourne *Argus*, 24 Sept., 1904. "The Geological Plan of Some Australian Mining Fields," *Science Progress*, 1906. p. 131.

[9] "Broken Hill Silver Mine, N. S. W.," Economic Geology, 1908, pp. 644–646.

[10] Geology of Broken Hill Lode," Geol. Surv. N. S. W., 1894, p. 92.

enlarged by the chemical action on its walls of the waters circulating within it."

Jaquet therefore appears to have perceived the great part played by replacement in the formation of the lode.

The Geological Sub-Committee[11] discussed four types of faults and stated the existence of an unconformity between the Broken Hill schists and the overlying tillite supposedly of Pre-Cambrian age.

Sir Douglas Mawson[12] separated the Torrowangee group from the older Willyama, or Broken Hill, series.

Dr. E. S. Moore described the lode as originating in a fault within rocks apparently of Archæan age.[13]

PHYSIOGRAPHY.

The region forms an undulating plateau lying about one thousand feet above sea level. A long line of fault of meridional disposition and of Cenozoic age has raised an area of 1,500 square miles of ancient rocks above the level of the plain which invests it on all sides. Thus it would appear that the famous Broken Hill lode might have escaped detection had it not been for the Cenozoic faulting and tilting.

GENERAL GEOLOGY.

The general geological features of the region will be treated as follows:

A. Rocks of Sedimentary Origin.
B. Rocks of Igneous Origin.
C. Rocks concerning the origin of which there is no consensus of opinion—"Quartzites."
D. Structural Geology.
E. Metamorphism.

[11] "Geology Broken Hill Lode," *Aust. Inst. Min. Engineers*, 1910, pp. 161–236.

[12] "Geological Investigation in the Broken Hill Area," Memoir, Royal Soc., S. A., 1912.

[13] ECONOMIC GEOLOGY, 1916, p. 237.

Rocks of Sedimentary Origin.

The rocks of sedimentary origin are grouped as follows:

I. Willyama Series—
(Sillimanite gneiss, mica schist, quartz schist, quartz mica schist, quartzite schist, chloritoid schist, sericite schist, staurolite schist.)

II. Torrowangee Series—
(Conglomerate, quartzite, tillite, limestone, marble, claystone.)

III. Mootwingee Series—
(Conglomerate, quartzite, sandstone, claystone and shale.)

IV. White Cliffs Series—
(Sandstone and shale.)

V. Post-White Cliffs Series—
(Sandstone, shale, uncompacted sands, alluvium of Great Plains, Kunkar, surface deposits of silica.)

Willyama.—The Willyama or Broken Hill Series consists of a group of ancient beds of mudstone, shale, limestone, together with sandstone of fine texture. The total thickness of all is considerable, and an interesting feature concerning these types is the close-spacing of the ancient bedding planes.

The criteria of the sedimentary nature of these altered rocks consist in part of their high content of sillimanite, and their general chemical composition, as determined by Mr. J. C. H. Mingaye and his staff, together with those of the Broken Hill Chemical Committee. Evidence is found also in the presence of abundant traces of planes older than, and in addition to, those of schistosity or flow cleavage and of fracture cleavage. These older planes were, in the first place, both parallel and sub-parallel to each other, but have suffered later distortion and dislocation. They are unevenly spaced, the normal distance between alternating planes being less than a quarter of an inch, and in no instance exceeding fifteen inches. Moreover, they have all the appearance

of bedding planes after due allowance has been made for the modification inevitable by close folding and by rock alteration. They formed surfaces of parting also for bands of rock consisting of minerals dissimilar both in shape and mineral composition. In many places traces of bedding planes have been obliterated by intense metamorphism, as in the case of the sillimanite gneisses or schists near Round Hill.

The Torrowangee, Mootwingee, and other sedimentary series of the district are not associated with the Broken Hill lodes, and lie at distances considerably to the north.

The age of the Willyama is considered to be Archeozoic, and the tillite overlying the Willyama is, stratigraphically, well below the lowest Cambrian fossils known in the South Australian district. The tillite may, therefore, be Pre-Cambrian.

Igneous Rocks.

These may be grouped as:

I. Sills and lenses between bedding planes—
   1. Gneiss.
      (*a*) Augen and platy gneiss.
      Sills and segregations of aplite.
      (*b*) Footwall gneiss.
      (*c*) Granulite.
   2. Amphibolite.
   3. Pegmatite and aplite of pre-lode period.

II. Lenses between bedding planes or as replacements of sediments, or crush-zones, derived from igneous emanations.
   (*a*) Magnetite lodes.
   (*b*) Garnet and rhodonite lodes.
   (*c*) Tin and wolfram lodes.

III. Sills and dikes—
   1. Granite of fine texture.
   2. Pegmatite of post-lode period.
   3. Serpentine.
   4. Dolerite.

The foregoing schedule supplies the names of the igneous rocks in chronological order of their entry. Of these, the types of No. I. exist in great numbers. They are sills, and no sign of their feeding source has been found despite the fact that diligent search has been made for them. On the other hand, when traced over considerable distances, they appear to have transgressed the bedding planes slightly, but in any section, say of half a mile, they appear to conform absolutely to the bedding planes. In the cross sections of the area, therefore, these rocks can be represented only as sills and pressure lenses without visible source of supply. Lodes come under a similar heading as do also the remarkable *lit-par-lit* forms of pegmatite occupying the center of the field.

The "granites" lie to the west of the area of maximum metamorphism. Their occurrence is that of sills in considerable numbers, with associated short apophyses or tongues, without dikes.

The serpentines conform to this type also, but are more lenticular.

Dolerite dikes cross the strike of the associated rocks, and they have no visible connection with bosses, sills, or other rock types exposed near the present surface.

The gneisses are confined in the main to the center of the field. They are of the primary type, this fact being appreciated first by Browne,[14] although Andrews had noted, and used in mapping, the knowledge that the peculiar gneissic flow arrangement was parallel to the bedding planes of the associated sediments, and that the later planes of schistosity were occupied by augen consisting, not of distorted feldspars, as in the case of the earlier flow, but of aggregates of silica and feldspar.

"Quartzites."

There is no consensus of opinion as to the origin of a series of rocks having a silica content exceeding 80 per cent., occurring in great quantities in the Broken Hill district, which are named "Quartzites," and which have the appearance either of sedi-

[14] E. C. Andrews, Broken Hill Report, Geological Survey, Dept. Mines, N. S. W., 1922. Appendix I. by W. R. Browne.

mentary beds or of sills. Browne considers that they are of igneous origin, but the author, from the field evidence, considers them as a group presenting peculiar difficulties, but explained better as sediments which have been highly altered, rather than as igneous sills.

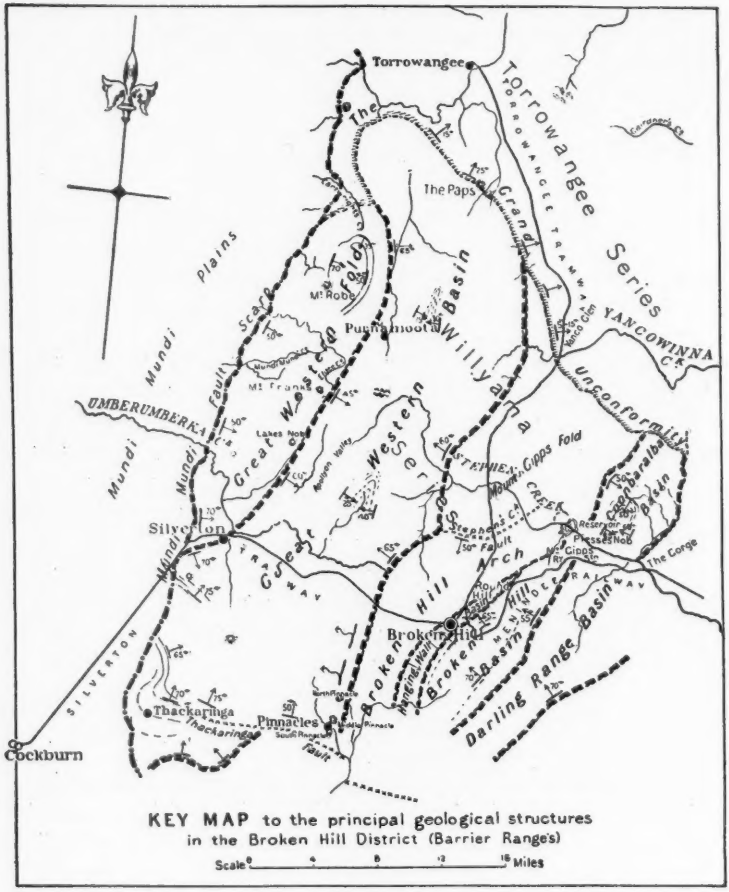


FIG. 48. Key map to the principal geological structures in the Broken Hill District.

Structural Geology.

The Key Map, reproduced here from the Broken Hill main report (Fig. 48), shows that the principal structures in the Broken Hill locality consist of structural basins of complex nature traversed in places by zones of rock flowage and of actual dislocation over very restricted lengths, both horizontally and vertically. One of the essential features in regard to these dislocations is the obliteration or disappearance of actual dislocation within short distances along zones of rock flowage.

The folding is of the close type, and the folds themselves appear to be of the shallow and isoclinal type, being ornamented by numerous secondary and tertiary forms.

Metamorphism.

Metamorphism in the Broken Hill district will, for convenience, be treated under the following subdivisions:

(1) Geographical distribution of the secondary minerals.
(2) The pegmatite "injections" of the central area of maximum alteration.
(3) Relation of metamorphism to Willyama folding.
(4) Relation of metamorphism to lode formation.
(5) Relation of metamorphism to Torrowangee folding.

Geographical Distribution of the Secondary Minerals.—(*a*) Minerals of Altered Sediments and Igneous Rocks. In the main the minerals indicative of intense physical and chemical action, such as abundant sillimanite with garnet, feldspar, and biotite, are arranged in sub-circular or confocal areas with foci lying along the zone containing the main Broken Hill lode. This statement, however, needs some slight modification. While it is true that the sillimanite area in the main is that of the central area of the field, a narrow strip of the sillimanite occurs along the western portion of the fold. In this relatively small area, however, the sillimanite is not as highly developed as in the central region.

The central area is characterized not only by a strong develop-

ment of sillimanite, but also by much garnet, biotite, feldspar, and quartz, these being intimately associated. In many places along the central, north, and south axes of the central area the altered sediments might be mistaken for igneous gneisses were it not for the presence of the great wealth of sillimanite by which they may be suspected as being of sedimentary origin by Bastin's important law.

Beyond this central area, as in the confocal belts to the east, north, and west, the sillimanite-garnet types are replaced by a wealth of andalusite, chiastolite, and mica-schists, with but little development of garnet. In the western extremity of the old folded shield, however, sillimanite schists outcrop, but without possession of the characteristic appearance and associations of the central area.

(*b*) Minerals of Ore Deposits. The geographical distribution of the lode minerals shows a remarkable interdependence of the agencies which produced both the regional metamorphism and the ore deposits.

The central area which is remarkable for this great development of sillimanite, garnet, biotite, feldspar, and pegmatite "injections," so called, is characterized also by the occurrence therein of ore deposits which consist of galena and zincblende, together with copper pyrites in small proportion, all within a gangue of manganese garnet, pegmatite with feldspar, fluorspar, apatite, gahnite, calcite, and quartz, with or without rhodonite.

It is interesting also in this connection to note that the lodes containing rhodonite occur within the center of the area of maximum alteration, whereas the types without rhodonite lie on arcs removed from the axis of greatest alteration. The rhodonitic area thus corresponds to that indicated by the maximum development of silica, garnet, and feldspar within the altered sediments.

A significant feature in this connection is the greater age of the sillimanite and garnet of the country rocks than of the ore deposits, thereby suggesting that the ore deposits are a revival or recrudescence of the action which caused the great alteration of the sediments at an earlier stage.

The galena lodes, which occur in a gangue of carbonate of iron, lie outside the area of maximum alteration, and occur chiefly within the area occupied in the main by mica, andalusite, and chiastolite schists. These include the Thackaringa, Silverton, Apollyon Valley, Purnamoota, and Day Dream Groups.

The tin-wolfram deposits occur typically with pressure lenses of greisen and pegmatite lying within a northern and outlying arc which in turn is situated beyond the silver-lead zone. The rock types within which the tin occurs are well-bedded phyllites, silky slates, and mica schists, of Willyama age.

Pegmatite Injections of the Central Area.—An interesting feature in connection with this central area of maximum alteration is the occurrence of innumerable "eyes," lenses, and narrow veins, of pegmatite developed along primary gneissic planes, and planes of schistosity. A great development of this material occurs also along the schist planes of the altered sediments. There is a tendency, further, for development along the more prominent examples of the bedding planes. This feature is relatively absent from the more massive types of sediments, but is remarkably abundant within the laminated sandstones and the banded gneisses of the aplitic and platy types.

Relation of Metamorphism to Willyama Folding.—The sandstone, clay, and shale belts, the gneiss, the less massive amphibolite belts, and the earlier pegmatite lenses and sills of the central area, have suffered the greatest alteration of the field. The earlier igneous types appear to have been folded since their introduction as sills into the altered sediments. On the major fold turns, very severe crushes and strains, or shears, have been formed whereby the sillimanitic, andalusitic, or micaceous, schist has been changed to a sericite type or to one with abundant quartz, mica, and garnet, or still again to one with abundant staurolite.

The augen gneiss and the pegmatite also may be changed to quartz sericite schist on these turning points of the folds as well as along the shear zones.

The simplest explanation of these features is that the great

sills of gneiss, amphibolite, and pegmatite were formed during a period immediately preceding that in which the pronounced and close folding had taken place.

Relation of Metamorphism to Lode Formation.—All the Broken Hill lode types are associated with zones of crush or shear.[15] The latter are younger than the typical sillimanite, andalusite, and chiastolite schists, the gneiss, the amphibolite, and the earlier pegmatite.

A considerable percentage of the secondary mineral growths in the crush zones are of the form of "augen," eyes, or thick, short lenses. The lode minerals, on the other hand, are fresh in appearance, the crystals have sharp edges, and they have been developed as a replacement of the crushed material and of the associated schists.

The earliest stage of development appears to have been marked by the growth of sillimanite, andalusite, chiastolite, or mica schist, the second of sericite, garnet, staurolite, and other minerals within crush zones of different ages. The lode development appears to have begun by the replacement, and entry otherwise, by magnetite.

Later stages were marked in succession by the development of pegmatite along zones of drag-fold and shear, with still later replacement by rhodonite, garnet, gahnite, chlorapatite, fluorspar, and other minerals.

Relation of Metamorphism to Torrowangee Folding.—The Torrowangee tillite, and other sediments which were supposed to be Pre-Cambrian, have suffered very little alteration, except locally, where the basal rocks of the series have moved differentially with respect to the Willyama schists during the folding of the Torrowangee Series.

TYPES OF ORE DEPOSITS.

The Broken Hill ore deposits are described as lodes. They are not, however, approximately tabular in form, lying between

[15] The term "shear" as used in this note implies readjustment by differential movement between rock particles by flowage over a considerable width rather than by dislocation along a narrow zone or plane.

well-defined walls and possessing definite dips, as true lodes or veins are supposed to possess. On the other hand, they are deposits of irregular form, which may arise either from the replacements of drag-folds associated with strain zones, or as the result of the replacement of the apices of close folds in the case of the great Broken Hill lode itself. Still another group has arisen as the result of the replacement of the apices of close folds of asymmetric form associated with shear zones. In these types, ore also occurs in the form of pressure zones developed within the shear or crush zone associated with the replaced apex of the close fold.

Table of Occurrences.

A. Productive Groups.

1. Silver-lead and zinc group.
   - (*a*) Galena with zincblende and traces of copper pyrites in a gangue of pegmatite containing green feldspar, rhodonite, garnet, gahnite, apatite, fluorspar, calcite, and quartz.
     Example: Main Broken Hill Lode.
   - (*b*) Types similar to (*a*), but without rhodonite.
     Example: Lodes within the sillimanite schist areas, outside the main Broken Hill Lode.
2. Silver-lead group.
   - (*a*) Galena with quartz with or without fluorspar.
     Examples: Lodes of the western portion of the Great Western Fold.
3. Silver-lead group without fluorspar.
   - (*a*) Galena with carbonate of iron and quartz.
     Examples: Lodes within the mica-schists which surround the sillimanite area to the west. These occur mainly in the western portion of the Great Western Basin and are associated with granite sills which are not gneissic, being short tongues or apophyses which penetrate the surrounding mica-schists.
4. Tin-wolfram deposits.
   These occur within a gangue of greisen and pegmatite with abundant tourmaline and halloysite. Amblygonite is present in some of the exposures.
   Location: These types occur within an arc extending from a point fourteen miles to the north of Broken Hill to one fifty miles to the north-north-west.
5. Platinum deposits.
   These contain the various platinoid minerals, together with cobalt, nickel, copper hematite, and quartz.

Location: An eastern belt within mica-schists containing subordinate sillimanite.

B. Non-Productive Groups.

1. Gahnite-quartz lodes.
   Location: Associated with Broken Hill types of lode in the sillimanite area.
2. Magnetite with garnet, apatite and quartz. Granular types.
   Location: The eastern portion of the sillimanite area.
3. Magnetite with hornblende and quartz.
   Location: Outside the sillimanite area. Minerals of this type are not finely granular, but are of irregular texture or are banded in a remarkable manner.

Structure of Main Broken Hill Lode.

The outcrop of the Main Broken Hill Lode exceeds three miles in length and passes under the alluvium at each end. The general appearance of the outcrop is that of two arcs of unequal size, the convexity of each being directed to the northwest. This outcrop is a continuous feature, but is markedly variable in size, being from one hundred to two hundred feet wide in places, and not exceeding a width of one to three feet at one point.

The footwall rocks within a distance of five hundred yards of the lode consist of the Footwall Gneiss, the Granulite, augen-gneiss, aplite gneiss, amphibolite, and altered mudstones, the latter being apparently the chemical and physical equivalent of the "kindly" black slate of some of the great mining fields of Australia.

The hanging wall rocks are somewhat similar to those of the footwall, but the Footwall Gneiss is absent, although the Granulite is present. The sillimanite schists and amphibolite sills are present in both walls, but they exhibit differences of appearance when contrasted.

A study of the map suggests that the lode is in a fault zone, but a close examination of the rocks affected indicates that this appearance has been caused by a drag-fold in the hanging wall, and a close folding of both walls, the latter being productive of local variations in the width of the outcrops of the country rock.

The dip of the lode is variable, but is mainly at a high angle in a westerly or northwesterly direction.

In plan, the lode has been shown to have the form of two large curves, which together form a persistent zone or belt.

In longitudinal section, the lode assumes the form of a long, flattish, but irregular arch, truncated abruptly above the surface and terminated below in a closed curve at the long central portion at a depth of five hundred feet from the surface, but pitching north and south thence in undulatory manner to the greatest depths yet worked, namely, eighteen hundred feet at the south. and fourteen hundred feet at the north end.

In cross section, the lode consists mainly of two portions, namely, a more or less persistent and common limb known as the Footwall Lode, occurring in a zone of silicified crush, and a compound form suggestive of one or several "saddles" springing from a common footwall lode. This compound form appears to be a drag-fold which has an undulatory pitch north and south, and which at one place may be approximately of the form of an asymmetrical anticline. In others it may be in the form of several "saddles" (Fig. 48) one above the other, while in other places still, it may assume the form of peculiar bulges or thickenings within the common footwall lode itself.

These hanging wall bodies conform in shape to those of the folds within the associated sillimanite schists, even at the points of greatest distortion and puckering.

The ore deposits disappear completely downwards, as commercial bodies, at the points of termination of the closed folds associated with the lower portion of the Footwall Lode.

An examination of the mine workings shows that the laminæ of the hanging wall have been dragged against the footwall with the production thus of differential movement between the two locally.

Mineral Association in the Main Broken Hill Lode.

If the lode in longitudinal section be considered as a long irregular arch with great approaches deeply intrenched, then the central portion of the arch must be considered, in the main, as an intimate association of lead and zinc sulphides within a gangue

of rhodonite, pegmatite with green feldspar, apatite, fluorspar, quartz, and silicified schist, whereas the great northern and southern approaches contain a calcitic content which is correspondingly emphasized by progressive decrease in the amount of rhodonite and garnet.

The pegmatite with green feldspar occurs throughout the length of the lode, both as lenses and as discontinuous patches. It does not occur commonly in the central portion of the arch, but is abundant in the northern and southern extremities. In places, as at the southern end, it may occur as long lenses sub-parallel to the main lode, and affecting the area distant from twenty to thirty yards to the west. It is associated almost invariably with lode material, having a garnet gangue. It appears as a forerunner of the lode proper, replacing the schists along the zone of strain and being replaced in turn by all the associated minerals of the lode.

The rhodonite contains a considerable percentage of iron oxide, together with lime. The garnet is a manganese variety containing considerable percentages of iron and lime also.

The main minerals of the lode occur as aggregates of crystals, and as granular and interlocking intergrowths, in which striking crystals of garnet, rhodonite, galena, and other minerals, are developed, all with clean and sharp faces, and moreover, showing no distortion such as might be expected to occur in forms developing under conditions of strain.

A variety of the garnet is a finely-granular form known as the "garnet-sandstone." This may occur scattered sporadically throughout the Broken Hill deposit, but it occurs also as great "chimneys" or "pipes" many hundreds of feet in length, and as much as fifty to one hundred feet in width. This peculiar development was found in the Junction, and Junction North, Mines.

In the British Mine, the rhodonite masses are overridden by the commercial bodies of galena and zinc.

The gahnite occurs in octahedra. It may be said generally

that the main development of this mineral has occurred in places lying a little outside the positions occupied by the lodes of lead and zinc.

Interesting occurrences are the zones of granular magnetite associated with manganese-garnet, chlorapatite, and quartz, developed within a zone, or zones, sub-parallel to the Footwall Lode. and distant about a quarter of a mile from the Main Lode.

The lode in the footwall zone consists in many places of siliceous ore in the form of "eyes" or lenses, both small and large, and which appear to be of the pressure type, that is developed by pressure between the bedding planes, forcing the latter apart to accommodate the growth of the introduced material. The great hanging wall bodies, however, as also the wider portions of the footwall deposits, show abundant traces of bedding planes within them, representing altered sediments. At places where the replaced beds are inclined at steep angles, and are in belts which are relatively narrow, the lode is impoverished, whereas at places where it is wide by reason of undulations or "wallows," it is correspondingly richer and larger.

Origin of Lode.

It would seem that a series of ancient silts and shales were deposited within the Broken Hill district; that these sank to great depths below the surface of the period considered; and that they were invaded by sills whose numbers are legion, and whose chemical and mineral composition is that of primary gneisses, amphibolites, and pegmatite.

At a subsequent stage, the beds, and the associated igneous sills, were closely folded and sheared within the zone of flowage. Igneous emanations appear to have arisen along the zones of strain in the region of rock flowage at a slightly subsequent stage. The majority of these appear to have passed vertically through the rocks now occupying the present surface of the district. Some, however, were trapped within a large and peculiar drag-fold. The latter is a portion of a closely-folded anticline which had suffered differential movement of the limbs through stretch-

ing by rock flowage. The rock type in which the ore emanations were trapped consists of laminated sillimanite schists, which had been laid down in the old Archean basin as thin laminæ of silt and shale.

No open space was developed during this folding, and the ore deposits were of the nature of replacements in the drag-folds, although partly in the form of "pressure lenses" within the main feeding zone of strain. The rising emanations appear to have left no trace of their passage through the rocks they traversed below the intersection of the drag-fold and the associated zone of strain. Action of this kind apparently finds an analogy, or homology, in certain types of contact deposits.[16]

A type of deposit which is slightly older than the Broken Hill Lode, but which falls within the same period of deposition, is exemplified by the deposits of magnetite with garnet, apatite and quartz, and lying several hundreds of yards to the southeast.

The pegmatite with green feldspar appears to have been formed within zones of strain at a date somewhat later than the development of the magnetite lodes.

Silica appears to have been continuously introduced during the whole period of lode formation.

Rhodonite, garnet, apatite, fluorspar, gahnite, and calcite appear to have been developed simultaneously by replacement, together with galena and zincblende, the rhodonite being formed by slight decrease of pressure. This explains the relative absence of rhodonite from the upper portions as well as the northern and southern ends of the lode. These minerals all entered subsequently to the formation of the pegmatite with green feldspar.

The garnet of the lode appears to be intimately related to the rhodonite. Each has a high content of manganese, together with a considerable percentage of lime and iron oxides. The rhodonite occurs only within the area or zone of maximum chemical and physical activity, whereas the garnet, in common with the pegmatite, magnetite, apatite, and gahnite, is not only asso-

[16] E. C. Andrews, "Molybdenum Industry in N. S. W.," Min. Resources, No. 24. Dept. Mines, 1916.

ciated with the rhodonite, but occurs at distances of miles beyond the range of deposition of that mineral.

The relation between the garnets of the lodes and of the country rock is one of considerable interest, inasmuch as it has been considered by some other observers[17] that the lode garnets are residuals of the country rock types.

In this connection it may be pointed out that:

1. The crystal forms of the two types are dissimilar.

2. The lode types have peculiar colors, lustrous faces, and they show no sign of distortion. The country rock types, on the other hand, are commonly in the form both of "eyes" and crystals within the zones of crush.

3. The garnet sandstone is granular and occurs either as sporadic patches and lenses, as pressure lenses of considerable size between the bedding planes, or as "pipes," many hundreds of feet in length and one hundred feet in extreme width in one example at least.

4. The garnets of the lode are not confined entirely to the area within which garnet is developed microscopically in the country rock.

5. The chemical composition of the two types is not similar.

6. The lode garnets are younger than the main crush or shear zones along which the garnets of the country rocks have been distorted in so many places.

The evidence then is that the country rock garnets, which are characteristic of the sillimanite schist, were derived during a period of regional metamorphism, by a mere rearrangement of the particles of the ancient mudstones and shales, without noticeable introduction of foreign material. On the other hand, the lode garnets represent another and later complete rearrangement by replacement of these ancient schists. There was, however, in this later phase, a notable introduction of foreign material, such as silica, manganese, iron, lime, lead, and zinc.

[17] J. B. Jaquet, "Geology of the Broken Hill Lode," p. 92. E. C. Andrews, Broken Hill Report, Geological Memoirs, N. S. W., Appendix II. by F. L. Stillwell.

It would appear thus that the garnets of the lode are not residuals of the country garnets, but that they represent a complete recombination of silicates under a revival of conditions of heat and pressure, similar to those which had obtained during the formation of the garnet, in the replaced portions of the sillimanite schist. The lode does not appear to be a replacement saddle in which the ore disappears gradually between bedding planes. On the contrary, the great commercial bodies of ore within the main Broken Hill Lode appear to be replacements of schists which have been closely folded, the same belt or folded country enveloping the ore body. Tapering lenses of the lode do occur, however, between bedding and schistosity planes within the Footwall body.

If the Broken Hill lodes be assumed to be true "saddles," then, in certain places along the main line of lode, there exist several individual saddle forms which appear to possess a common leg or limb. These would imply the existence of a fault or a drag-fold aided by rock flowage.

Age of the Ore Deposits.

The Torrowangee Tillite at The Sisters contains numerous erratics of local magnetite from the Willyama.

Howchin[18] considers the tillite to be Lower Cambrian, but there is a growing opinion amongst geologists that this deposit is of late Pre-Cambrian age.

The magnetite appears to belong to the period in which the Broken Hill Lode was formed, and the existence of Pre-Cambrian tillite with erratics of Willyama magnetite, together with the general assemblage and appearance of the igneous and sedimentary rocks containing the magnetite, suggests the age of the great Broken Hill Lode to be Archean.

SYDNEY, NEW SOUTH WALES,
AUSTRALIA.

[18] "The Geology of South Australia," 1918, pp. 339–355. Govt. Printer, Adelaide, S. A.

SOME ETCHING TESTS ON PYRRHOTITE.[1]

H. C. BOYDELL.[2]

In the course of determination of minerals in polished sections the writer has often been perplexed by the variability of the results of microchemical tests given by the same mineral, frequently by the same polished surface of the same specimen. In consequence he decided to carry out a series of tests in order to compare the results given:

(*a*) By the same mineral from different localities;
(*b*) By different surfaces of the same specimen; and
(*c*) The proportion of positive to negative results over a large number of microchemical tests of the same mineral.

The mineral chosen for the purpose was pyrrhotite, this giving more or less varying results when polished sections of it are tested microchemically. Four specimens were ground, polished, and tested. One was from Sudbury and had what appeared to be a natural etch surface. In addition to pyrrhotite, it also contained pentlandite and chalcopyrite. Three surfaces of this specimen were prepared, one parallel to the etch surface, and two perpendicular to this and to one another. Another specimen from near Newton Stewart, Scotland, had one surface prepared. This also contained chalcopyrite, pyrite, and pentlandite. A third, from Bodenmais, Bavaria, showing a parting parallel to the basal plane, had three surfaces ground and polished, one parallel to the parting, and two at right angles to this and to each other. In addition to pyrrhotite, chalcopyrite, blende, and quartz were present. The fourth specimen examined was from Pike Hill, near Corinth, Vermont, and for this two polished surfaces

[1] Presented before the Society of Economic Geologists, Amherst Meeting, Dec. 28, 1921.

[2] Introduced by Waldemar Lindgren.

were prepared perpendicular to one another. Besides pyrrhotite, blende, quartz, and chalcopyrite were also present. Care was taken to obtain surfaces as well prepared, polished, and free from scratches as possible.[3]

The microchemical tests used were the determinative ones given by Davy and Farnham in their "Microscopic Examination of Ore Minerals," and the strength of the reagents was as recommended by the same authorities. The method of applying the tests was to place a drop of the reagent in contact with a portion of the polished surface of the mineral included in the field of the microscope (a 16 mm. objective being used). This was allowed to remain in contact for three minutes, then replaced by a drop of water from a dropping bottle, and the surface was dried with absorbent paper, preferably by applying it at one side of the wet spot rather than by "mopping." For this purpose filter paper was found most suitable.

In all, 136 microchemical tests of all kinds were then applied to the nine polished surfaces of the four specimens. The results of these tests were classified as positive (*P*), indefinite (*I*), and negative (*N*), according to whether the mineral was (*a*) decidedly, (*b*) uncertainly or only very faintly, or (*c*) not at all tarnished, respectively, by the drop of reagent.

This classification was also applied to the action of the fumes of the reagent (liberated from the drop itself either when being applied or after being applied to the surface). The detailed results are given below:

BEHAVIOR OF PYRRHOTITE FROM DIFFERENT LOCALITIES.

With HNO_3.—All the specimens gave a positive reaction, *i.e.*, were tarnished with or by the fumes, the color of the tarnish ranging from a decided brown to a faint discoloration of the surface only. The action of the drop of reagent itself was doubtful with two and negative with two of the specimens. The indefinite reaction here, in view of the fact that fumes generally

[3] The first and second of the specimens were kindly supplied by Professor Charles Palache of Harvard University.

produce tarnishing, probably means that the acid attacked the mineral, but that the products of the reaction were soluble in the acid.

With HCl.—The action of the fumes was generally negative, as also was that of the liquid reagent. The drop, however, was always colored yellow at the end of the three minutes, so that reaction must have taken place, though no other visible evidence of it was left.

With KCN.—Three of the specimens were definitely unaffected by the fumes, and the other varied in its behavior. In contact with the drop, one gave positive reaction, one negative, and the other two indefinite results.

With $FeCl_3$.—One specimen was negative to the fumes, one was positive, and the other two varied. The drop gave positive results with one specimen, and more or less indefinite results with the other three.

With KOH.—Three of the specimens were definitely negative toward the fumes, and the other one was more often negative than positive. All the specimens were definitely positive to the liquid reagent, the drops in many cases became light brown in color toward the end of contact with the surface.

With $HgCl_2$.—One specimen was negative to the fumes, one was positive, and the other two were much oftener positive than negative. With the liquid the specimens gave indefinite results, though none of them were negative.

THE INFLUENCE OF DIFFERENTLY ORIENTED SURFACES OF THE SAME SPECIMEN.

Etch Surface.—This existed in the Sudbury specimen. The polished surface prepared parallel to it, while showing some differences in results both as compared with the other surfaces on itself and also with the aggregate results from all the specimens, did not do so to a sufficient extent, nor were the tests sufficiently numerous to allow of an opinion being expressed as to whether any essential difference in results of microchemical tests can be expected on etch surfaces under the conditions of polished section

mineral work. Here the question arises as to whether the preparation of the polished surface may not alter the molecular condition or, perhaps more correctly, the atomic structure of the original etch surface. A disadvantage connected with this particular specimen was its great brittleness, so that in preparation it became greatly reduced in size, hence the polished surfaces were small.

Parting Surface.—The parting surface, present in the Bodenmais specimen, is, in pyrrhotite, developed most distinctly parallel to the basal pinacoid.

In this case the results generally conformed to the aggregate behavior of pyrrhotite to the different reagents. A large number of repeated tests would be necessary to show whether these differences are persistent, but the evidence obtained would seem to point, in the writer's opinion, to their being of a minor and unimportant character.

Surface of Chance Orientation.—The Sudbury specimen had two of these prepared, the Bodenmais two, the Newton Stewart one, and the Pike Hill two, or a total of seven such surfaces were tested.

Here again, while differences in results exist, they would seem to be of the general character that are met with in polished section mineral work, and over a large number of repeated tests the results in different faces of the same specimen, and in different specimens, would probably conform to the aggregate behavior of pyrrhotite to microchemical tests.

AGGREGATE RESULTS OF THE TESTING.

From the results obtained pyrrhotite may be said to give the following microchemical reactions:

With HNO_3.—*Fumes*—Positive reaction.
Liquid—Indefinite to negative results.
With HCl.— *Fumes*—Negative results.
Liquid—Indefinite to negative results.
With KCN.— *Fumes*—Negative results.

Liquid—More often positive than negative results. Indefinite results as often as negative.

With $FeCl_3$.— *Fumes*—Rather more frequently positive than negative.

Liquid—Indefinite results most frequent—positive results, however, much oftener than negative.

With KOH.— *Fumes*—Negative results.

Liquid—Positive reaction—this is the most definite microchemical test (of those used) for pyrrhotite, provided that sufficient time (3 minutes) is allowed for it to develop.

With $HgCl_2$.—*Fumes*—Positive results more frequent than negative.

Liquid—Indefinite results prevalent, but no absolutely negative results.

In connection with the $HgCl_2$ test, there was a definite tendency for the tarnish to take the form of a ring of varying width corresponding to the edge of the drop. This may have been due to adsorption and possibly may have been the cause of the tarnish attributed to the action of fumes only. Owing to the $HgCl_2$ solution used being a saturated one (as is recommended by Davy and Farnham), there was a tendency for the drop of liquid while in contact with the mineral to become cooled, therefore, supersaturated, and to deposit crystals on the surface. These sometimes flashed into existence, in other cases they were seen to grow like tiny pins in the field of vision, the growth always being noticeable in the direction of length, and not of width. The appearance of crystals of $HgCl_2$ applies to the microchemical testing of all ore minerals with the reagent, and not to pyrrhotite alone.

According to Davy and Farnham,[4] the reactions should be as

[4] *Loc. cit.*

follows: "HNO_3 tarnishes very slowly faint brown; almost negative; rubs clean. Fumes tarnish brown. HCl negative (fumes sometimes tarnish faintly). KCN negative. $FeCl_3$ negative. $HgCl_2$ negative. KOH slowly tarnishes brownish or iridescent; rubs to brownish iridescence."

According to Murdoch,[5] the reactions should be as follows: "HNO_3 negative; slowly very faint brown. Fumes tarnish slightly. KCN negative. HCL negative; fumes quickly tarnish. Hot HCl tarnishes quickly, then blackens. $FeCl_3$ negative. KOH slowly tarnishes brilliant iridescent colors, persistent.

INFLUENCE OF PRELIMINARY CLEANING OF THE SURFACE BEFORE TESTING.

The specimen used was the Bodenmais pyrrhotite and a massive sample of arsenopyrite from Siegen, Prussia. The usual tests were made both before and after cleaning. The latter operation consisted of washing the polished surfaces with (*a*) HCl, (*b*) water, (*c*) KOH, (*d*) alcohol, and (*e*) ether. The results showed that the cleaning had but little, if any, influence.

In the course of polished section mineral work there is frequently encountered the apparent anomaly of the fumes from the reagents tarnishing a mineral, but of the liquid reagent giving no tarnish. This has been previously referred to under the testing of pyrrhotite and may be explained by the product of the reaction being soluble in the reagent or in the wash water applied to remove the former. The use of wash water, when it dissolves the fume tarnish, may usually be obviated by removing the reagent with a narrow pointed strip of filter or blotting paper, as has been recommended by Bastin. Solubility of the product of reaction in the drop of reagent also explains the frequent coloring of the latter, while no visible effect is left on the mineral surface itself.

SUMMARY.

In conclusion, the writer would emphasize the necessity in polished section mineral work of repeating each test on a mineral,

[5] "Microscopic Determination of the Opaque Minerals," John Wiley Sons, 191, p. 76.

not on the same spot, if it be possible to avoid this, but on several portions of the polished surface of the mineral in question. The larger the number of repetitions the better, if the reactions are found to vary much. In this way the results, which on the average constitute the aggregate behavior of the mineral to the microchemical tests, are most likely to be obtained.

LABORATORY OF ECONOMIC GEOLOGY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

DISCUSSION

AND

INFORMAL COMMUNICATIONS

GEOLOGY OF THE BRADEN MINE.

Sir: In the admirable paper of Messrs. Waldemar Lindgren and Edson S. Bastin on the Geology of the Braden Mine, which appeared in the March–April issue of this journal, the authors express the belief that the main primary sulphide mineralization formed large bodies of mineralized material with a copper content averaging considerably less than 1.5 per cent.—in most places of between 0.5 and 1.5 per cent., though locally slightly richer. Further, that their enrichment by descending secondary mineralization was necessary to raise their copper content to a workable grade, and that this further necessary mineralization was accomplished subsequently by descending surface waters. Thus by virtue of this process of secondary, or downward enrichment, these large bodies of 1.00 to 1.25 per cent. material, formed during the main primary mineralization, were brought up to 1.5 to 4.0 per cent., or even higher, in copper, rendering them commercially workable.

While it is believed by the writer that secondary enrichment added very materially to the size and value of these deposits, still it is also believed that even without this chalcocite enrichment, and due to the primary deposition principally of chalcopyrite, there would have been developed very large bodies of commercially workable ore of a content of 1.5 per cent. or higher in copper.

Evidence for this belief is found in study of the ore minerals throughout the mine workings at different horizons. In the higher levels of the mine, oxidation and secondary enrichment are, as a rule, more pronounced than in the deeper workings.

The higher ground appears to be more open, or pervious; to contain a relatively smaller percentage of pyrite, quartz and tourmaline than chalcopyrite as matrix or vein material. In driving the workings deeper, much more ground water was encountered, indicating that these deeper ores had been better protected from oxidation by the original water level, so that little chalcocite enrichment seems to have taken place below the recent ground water level.

In the higher workings chalcocite coats most of the chalcopyrite-pyrite ore as films and fills minute fractures. Dr. Berkey, of Columbia University, prepared many slides of these minerals and ores for study with the petrographic microscope. These studies showed that the chalcocite films were quite superficial, or of minor importance, and that the major portion of the copper was clearly to be credited to the chalcopyrite. Field study with the pocket lens had indicated this.

As a guide in forming an opinion of about how much weight to attribute to secondary enrichment at different horizons, samples of the ores, and of the ore minerals free from gangue, were collected from workings at various depths throughout the ore bodies. These samples were carefully analyzed and the results "recast" into their probable minerals. The results obtained from this work indicated that as an average not more than 25 per cent. of the copper could probably be in the form of chalcocite, even in the upper zones of most pronounced enrichment; that in the deeper zones it was considerably less, perhaps not more than 15 per cent.; and in the deepest parts of the ore body practically negligible.

The analyses and recasts therefore seemed to bear out the visual study.

To illustrate the importance of this chalcocite enrichment on the Fortuna, or Southern ore body, the following results are tabulated:

In this respect it is believed that the fully developed Fortuna ore body may be taken as representative of the others, though the Teniente and Regimiento are not yet fully developed.

EFFECT OF SECONDARY ENRICHMENT ON THE FORTUNA ORE BODY.

Ore Body Horizon.	Approx. Average Distance Below Surface Croppings.	Percentage of Copper in Form of Chalcocite Indicated.	Average Assay Value of Ore—Per Cent. Cu.	Average Assay Value Subtracting Chalcocite Enrichment—viz., Per Cent. Cu Prim. Sulphide Ore.
Fortuna 2 Adit to top of Sulphide Zone	160 ft.	Perhaps 30%	3.20*	2.24
Fortuna 2 Adit	500 ft.	20%	2.50	2.00
Fortuna 3 Adit	800 ft.		2.42	1.94
Fortuna 3½ Adit	1,000 ft.	15%	2.26	1.92
Fortuna 4 Adit	1,250 ft.	Negligible	1.88.†	1.88

* The samples of workings running up from Fortuna 2 level to the oxidized "capping" contained considerable copper in the form of oxides and carbonates as well as chalcocite, and although assays were made separately for the two former as well as for the latter, the average results were somewhat uncertain.

† The ore developed on the Fortuna 4 level was fresh and bright, showing no indication of oxidation or chalcocite enrichment. Here the ore body was constricted to a comparatively small area.

From thorough study of these deposits the writer believes that chalcopyrite is the chief mineral of value; that it dates back to the period of intensive mineralization following igneous activity, and is, in that sense, primary or original. Further, that this primary mineralization was sufficiently concentrated to form large ore bodies of workable grade, viz., 1.5 to 2.0 copper. Secondary chalcocite enrichment has certainly materially enhanced the richness of most of the ore, and probably has added somewhat to the expansion of the ore bodies, but it is not believed that to this process is beholden the chief value of these great deposits.

Believing in this interpretation, it was therefore necessary to seek an explanation in other causes of the failure of workable ore to continue to greater depth.

Primarily it is believed that such failure is due to an insufficient deposition of chalcopyrite per volume of rock at these greater depths. Had such deposition been as concentrated as that found above, deeper ground would probably have carried

from 1.5 to 2.0 per cent. copper, without any chalcocite enrichment. That the primary sulphide deposition was less intense was probably due to the less favorable condition of the deeper ground. It is generally much "tighter" or more consolidated, is less altered, and compared to chalcopyrite shows a larger proportion of quartz, tourmaline, and even pyrite as matrix and vein material. It is also possible that at greater depths, the mineralizers being under greater heat and pressure, selective deposition was differently governed. The mingling of the rising hot mineralizers with the cooler upper rocks and ground waters would thus have found a horizon above which heavy deposition of the copper-bearing sulphides was broadly favorable. If at this horizon the ground was also highly shattered and pervious to the passage of the mineral-bearing solutions, it would then afford a most favorable locus for the deposition of the ore. The writer believes this to have been the case.

In that part of the paper referring to a third period of mineralization, it is of interest to add the mineral ankerite to the list of conspicuous carbonates present. Ankerite is a member of the mineral group of rhombohedral carbonates and with a normal composition $Ca_2MgFe(CO_3)_4$. This mineral was prominently associated with the "Bornite" ore body developed in Fortuna 4. Analysis of crystals of this gave the following results:

CaO	30.26%
Fe	9.35%
MgO	12.60%

plus less than 1% each of SiO_2; Al_2O_3; K_2O; and Na_2O.

The specimens were usually of a grayish or yellowish cream color, and in close association with the bornite made strikingly attractive ore.

As the authors prominently listed the mineral siderite but made no mention of ankerite, it seemed that possibly the latter had been classed as the former.

ROBERT MARSH, JR.

4 WEST FORTY-THIRD ST.,
NEW YORK CITY.

REVIEWS

Petroleum: A Treatise. By Sir Boverton Redwood, Bart. Fourth Edition. London, Charles Griffin & Co., Ltd.; Philadelphia, J. B. Lippincott Co., 1922.

In earlier editions, Redwood's "Treatise" has firmly established its place as a classic in the science and industry of petroleum throughout the world; no higher compliment, therefore, need be paid to the present revision than to call it a marked improvement over the third edition (1913). "Encyclopedia" is the only word that seems to do justice to the scope of a work which deals so keenly and exhaustively with every phase of its subject.

Just before his death, in June, 1919, Redwood handed to the publishers copy for the greater part of the new edition which he and a number of collaborators had prepared during the latter days of the war. The almost completed task was taken up by his colleagues and carried forward through its final stages. It is obvious that a work of such magnitude, requiring many months for type-setting, proof-reading, and printing, cannot be absolutely "up to the minute," but every effort was made to include all available facts. The work is complete through 1918, somewhat less thorough for 1919, and contains many data for 1920.

Section I. ("Historical Account of the Petroleum Industry") now contains descriptions of about fifty countries; half a dozen countries and provinces have been added to those previously described, and new accounts have replaced many of those found in earlier editions. For the United States there is added a chapter on "The Unmined Supply of Petroleum," with a table of estimated reserves in January, 1919. Wyoming, which in 1918 produced 38,500,000 barrels, is transferred from the ranks of "minor fields" to its proper place among the more important states, and many new fields in this country are added to the lists. For American oil-men perhaps the most interest, among foreign countries, is attached to the new descriptions of Mexico, South America, Rumania, Persia, and Mesopotamia.

Section II. ("The Geological and Geographical Distribution of Petroleum and Natural Gas") is made up of two quite distinct parts. The second part, which has been carefully revised, shows the geographic distribution and the stratigraphic relations of the known oil and gas deposits and seepages throughout the world, and includes even more countries than Section I. To these descriptions have been added several new and

valuable maps, among which is a large four-sheet map of the oil and gas fields and pipe-lines of the United States (originally issued in 1917 by the U. S. Geological Survey). The first part of Section II., which is in a sense an introduction to the main body of the section, is made up of miscellaneous information about the mode of occurrence of petroleum and allied substances; this part has not been changed since the third edition, and is the least satisfactory chapter of the "Treatise." These sixteen pages, together with seventeen more in Section IV. (Origin of Petroleum and Natural Gas), contain practically all of the more purely scientific petroleum geology presented in the entire work. It would be difficult at best to crowd into less than three per cent. of the "Treatise" an adequate outline of the theories of origin, migration, and accumulation, but the difficulty is enhanced by too lengthy summaries of the views of Orton, Lesley, and other pioneers. Our science is moving forward with great strides, and recent studies of porosity, modern ideas of the effect of capillarity and of movements of underground waters, the several explanations for the relative content of "mountainward" and "basinward" structures, the relations between oil deposits and ancient shore-lines, and calculations as to the rate of exhaustion of various fields, are among the types of investigation that are constantly changing and molding our conceptions. Many such theories, though worthy of mention, have been put forward too recently to be included in the "Treatise," but there is no such good reason for the omission, among other views, of David White's suggestion as to the relation between the occurrence of petroleum and the carbon ratio of associated coals, a theory which was published in 1915, incorporated in a widely read book in 1916 and has been much quoted since that time. This part of Section II., then, although good as far as it goes, is inadequate and needs thorough revision.

Section III. ("The Physical and Chemical Properties of Petroleum and Natural Gas") is comprehensive; some five or six pages have been added, containing chiefly details of various crude oils, an account of optical activity, and several tables of the calorific values of petroleum and petroleum products.

Section IV. ("The Production of Petroleum, Natural Gas, and Ozokerite") deals minutely and at great length with every phase of the technical work of bringing oil and gas to the surface. Revision has added a newer and more complete list of all equipment for drilling deep wells, a valuable article by Arnold and Garfias on exclusion of water by cementing, recent development of the rotary method in Russia, methods of raising oil by compressed air as practised in Russia, Trinidad, and California, and many other valuable discussions. Under the heading of Galicia there is a brief reference to diamond drilling, a method which, as indicated by recent results in Mexico, may have much wider application in future.

In the concluding remarks of the section is quoted a paragraph from A. B. Thompson on attempts to increase the yield of oil by flooding with water or pumping air into nearly exhausted oil-sands; this brief mention of a subject which deserves more lengthy discussion might easily be overlooked because of the poor heading.

Section VI. ("Refining of Petroleum") is a full and excellent summary of the methods of refining. The general description is followed by an account of methods used in the United States and half a dozen other countries. Many additions to this section are found in the latest revision, of which possibly the most important are descriptions of topping plants in Trinidad and California, several new "cracking" processes, methods of compression and absorption for getting gasoline from natural gas, and a list of all refineries in the United States at the close of 1918, with the location and capacity of each.

Section VII. ("The Shale-oil and Allied Industries") contains enlarged descriptions of the oil-shale deposits in Scotland, France, New Zealand, New Brunswick, and several other countries, and new accounts of deposits in the United States, Newfoundland, Sweden, Finland, and Bulgaria. The extensive outline of methods and apparatus in the third edition is supplemented by a brief description of the Oakbank retort, patented in 1915.

Section VIII. ("The Transport, Storage, and Distribution of Petroleum") has been thoroughly revised, among the most important additions being a list of pipe-lines in the Mid-continent and California fields, new types of oil-carrying steamers, a description of the Foamite system of fire extinguishers for tankers, a discussion of the use of lightning conductors around storage tanks, and new details of tanks and their apparatus.

An almost endless list of devices for testing petroleum, petroleum products, and allied compounds, is contained in Section IX. New forms of dephlegmators, new methods of testing "motor-spirit" and of detecting and estimating the sulphur content of crude petroleum, a description of Dow's asphalt penetration tester and Philip's demulsification tester, and the specifications of the U. S. Fuel Administration for water-white kerosene and long-time burning oil, are among the many additions that were made in the excellent revision of this section.

Section X. ("The Uses of Petroleum and its Products") includes new chapters on the uses of switch and transformer oils, and of natural gas, the development of the natural-gas gasoline industry, and descriptions of several late types of burners.

Section XI., on the laws and regulations affecting the petroleum industry throughout the world, Appendix A, which contains mostly statistics on production, and Appendix B, which shows the import duties levied

on petroleum in practically all countries in the world, have been extensively revised and brought up to date.

Nearly nine thousand references are contained in the bibliography which forms the final section of the book. Unfortunately this list has not been enlarged since the third edition, and thus loses much of its value. In the preface the failure to extend the bibliography is explained by the high cost of type-setting, but possibly judicious pruning of the old list might have permitted modernization without an increase in the number of titles.

The "Treatise" is written throughout in clear and easy style. Its plan is logical and in general is consistently followed, although in a few places discussions seem to have strayed from their proper sections. Possibly a combination of Sections I. and II. would be an improvement, as it is somewhat inconvenient to look in two sections for details concerning a single country. Certain inconsistencies have crept into the book, probably due to its final revision by several collaborators; among these may be mentioned the lack of uniformity in the use of specific gravity and Baumé readings, for in some places one is given, in some places the other, and in some places both.

To those who from any standpoint are interested in petroleum the value of the "Treatise" is beyond question. No other book can be fairly compared to it, for while some other books of more limited scope may excel it in their own fields, no other combines such range in its subject matter with such exhaustiveness in detail. The "Treatise" is not the last word for any one phase of the petroleum industry, but it includes in handy form a wealth of information that otherwise could be secured only by long and patient search through a well-stocked library.

JULIAN D. SEARS.

Abriss der Lehre von den Erzlagerstätten. By RICHARD BECK AND GEORG BERG. Berlin, 1922. Published by Gebrüder Borntraeger, price, $3.60. 408 pages with 144 figures.

It appears from the preface to the present work that Professor Beck, for some years before his death, had in mind the preparation of a one-volume textbook that would bring within the reach of students of mining schools and of students of general geology, the essentials of the well-known three-volume third edition of his "Lehre von den Erzlagerstätten." He left no manuscript for this work but had sketched his plan in some measure by oral communications to his colleagues and by annotations in a copy of his larger treatise. Before his death he had expressed the wish that either Dr. Berg or Professor O. Stutzer might undertake the preparation of the present volume. The task fell to Dr. Berg, a former student of Beck's, and has been very capably carried out.

Condensation has been effected by some slight changes in classification and by the omission of details concerning the less important or less characteristic examples of the various types of deposits. On the other hand, the work is well illustrated and has been brought more nearly up to date than the last edition of Beck's "Lehre." Descriptions of some of the most important ore deposits in the United States are either lacking or so brief as to seem inadequate, but the American student can make up this deficiency from some of the good textbooks recently published in this country.

The text appears to have been almost wholly rewritten, so that it is generally consistent and well proportioned. On the whole, the book is an excellent one and deserves translation into English. Among the very few typographical errors noted was the amusing Teutonic variant *New Yersey*.

F. L. RANSOME.

Radium, Uranium and Vanadium Deposits of Southwestern Colorado. By R. C. COFFIN and others. Bull. 16, Colorado Geol. Survey, Denver, 1921. 231 pp., 53 figures and 4 plates (3 maps).

Mr. Coffin's report covers the geology of the radium deposits of Colorado, which lie in Mesa, Montrose, San Miguel, Dolores and Montezuma counties, and are included in an irregular area lying adjacent to the Utah line from Gateway on the north to a point south and west of Cortez, to date by far the most important known radium-bearing region.

The area is part of the high semi-arid to arid Central Plateau, deeply and precipitously dissected by numerous watercourses and cut by faults that have left steep escarpments hundreds of feet high.

The work is the first to cover what may properly be called the Paradox carnotite region. In gathering the data for it Mr. Coffin was assisted by a number of students and teachers of the University of Colorado, and this work occupied the whole or part of the summers of 1914, 1915, 1916, 1918 and 1919—a period that allowed rather extensive observation of mine operations and development. Plate I. is an excellent geologic map of the area, in part hachured.

The report is divided into six chapters, of which the first, "Geography," by P. G. Worcester, adequately covers the field. The second chapter, "General Geology" (pp. 28–124), 97 pages, is the longest, and is almost wholly devoted to stratigraphy. The great amount of field labor required for this chapter is scarcely to be appreciated by one who has not traversed the area or undertaken some similar work.

The rocks of the area range in age from Pre-Cambrian (schists and gneisses) to the Cretaceous (Mesa Verde shale), and in Paradox Valley

the beds show a thickness of about 2,400 feet above the gneiss and below the Muesa Verde shale. They are predominantly sandstones and shales.

The schists and gneisses are visible only in a few canyons. The Carboniferous rocks likewise are exposed only over small areas. They are greatly folded and very gypsiferous. Massive beds of gypsum are thought to be of Pennsylvanian age.

The "Red Beds" are treated together as the Permo-Triassic. The Permian (?) beds range from

> "the finest of maroon shales in the Paradox and Gypsum Valley sections to the coarse arkose conglomerates of lower Dolores River, where the beds contain boulders up to 1½ feet in diameter. These conglomeratic beds are comprised of almost every material found in the pre-Cambrian complex of the Uncompahgre Plateau. The most common type of boulder is derived from a granite characterized by large phenocrysts of pink to red feldspar. These materials with types of schists and gneisses in almost every stage of decay, make up the bulk of these beds."

The conglomerate is evidently a piedmont stream deposit, and is lightly consolidated. His next sentence naturally applies closely. "Quick lateral and vertical changes in the character of beds is typical of this formation." Although Mr. Coffin does not mention it, this deposit apparently occupies the same position as the Shinarump conglomerate farther west. Nowhere in the area was the Shinarump conglomerate recognized as such, though the "saurian conglomerate" of Cross at the base of the Dolores seems to occupy a similar position. The Shinarump conglomerate has a wide distribution through an area a hundred miles or less west of the Colorado-Utah line. The main interest of the Permo-Triassic (Cutler and Dolores) sandstones in relation to the radium deposits is that they contain one or two members that are thick enough (80 to 300 feet) and massive enough to be mistaken by the unknowing for the thick La Plata sandstone which underlies the carnotite beds. Though usually red, the Permo-Triassic beds are in some places white.

The La Plata (Jurassic) beds consist mainly of a massive cross-bedded cliff-forming sandstone 100 to 300 feet thick that forms one of the principal obstacles to travel. It weathers into characteristic smooth rounded faces known to prospectors and miners as the "slick rock" or "slick rim." It is generally pink in the lower part and whitish above. Below the massive sandstone is a greater thickness of thin cross-bedded sandstones that rest on the heavy red sandstone of the Dolores.

No roscoelite is found in the area covered by this report, and limestone is found in only one small patch, although near Placerville, 40 or 50 miles east of the carnotite region, the upper heavy La Plata sandstone is divided by a limestone bed, and roscoelite deposits are found just below the limestone.

The McElmo beds are the host rocks of the carnotite deposits and rest on the massive La Plata sandstone. They have a minimum thickness of 500 feet in McElmo Canyon and a maximum thickness of 900 feet at points within the northern half of the area examined.

Mr. Coffin's description hardly gives one an accurate idea of the general appearance of the McElmo as seen in the field. At the top is a mass of green and red sandy shales containing thin beds of sandstone and some conglomerates, the whole 300 or 400 feet thick, weathering into comparatively smooth slopes; below are the more massive sandstones, one to three of them, each 20 to 35 feet thick, that carry the carnotite, and generally separated from each other by sandy shales. Below these beds are in most places 220 to 250 feet of more or less thin-bedded sandstones, in some places shaly, referred to by Mr. Coffin as "shale beds," a misleading term, for only locally are they at all pure clay. His sections on pages 88 and 89 are the most typical. He speaks (p. 92) of limestone at several places in the McElmo, but it is nowhere fossiliferous.

In the sandstone at many places are masses of sandy clay of irregular outline. Gypsum is common in the sandstones, but this is true in most if not all arid or semi-arid regions. Fossil trees are abundant from a point 100 feet above the base to the top of the formation and some trunks attain a diameter of 8 feet. Imprints of reeds are common, and lignitic material is found in small pieces at many places. Bones occur at many places with the same vertical distribution as the wood.

Mr. Coffin believes that "the McElmo formation was deposited in lakes and on flood plains across which streams were continually altering their courses. The surface upon which the sediments were deposited was a smooth plain which was so near base-level that it was the site of deposition rather than erosion. Deposition did not take place evenly over this plain but beds were formed in many places only to be destroyed by shifting streams and deposited elsewhere. Fragments and lumps of shale inclosed in sandstone are evidence of such destruction.

"The flood-plain phase of deposition is emphasized further by the presence of ancient stream channels, the thinning and wedging out of individual beds, and the inclusion of lenses of fine material by coarse material. The type and extent of cross bedding, and the undulating and scoured surfaces which generally separate beds of shale from beds of sandstone, are further evidence that many of these beds are the result of stream deposition. . . .

"Inland lakes doubtless existed at different times over large areas of this plain and were the scene of the deposition of the even-bedded and the finely banded sandstones. Streams supplied materials of different sorts to different parts of this McElmo plain. . . .

"Although it is probable that many of the pieces of wood were carried to their present positions, the arrangement and abundance of plant fragments in several localities would not suggest such transportation. The partial evaporation of isolated lakes wherein gypsiferous soil may have

accumulated is not inconsistent with the conditions postulated. The remains of dinosaurs, presumably of semi-aquatic habits, are suggestive of climatic conditions and the flood-plain idea of the formation of these beds."

To my mind, the stream idea is untenable when carried to such a length. I have tried hard but without success to find stream channels. Why fragments of wood should not be carried in large quantity to any shore is not clear. The author thinks that the source of the material was somewhere in the west, but gives no reason for this belief.

Above the McElmo formation is 100 to 200 feet of conglomerate, sandstone and shales that Mr. Coffin thinks is below the Dakota and which he calls "post-McElmo formation." Above this is 100 to 200 feet of Dakota sandstone carrying coal at several places. In this isolated region this coal is a real blessing.

Intrusive rocks are confined to Ute Mountain at the south end of the area and to the north side of Disappointment Valley. No connection with the carnotite deposits can be traced.

Chapter 3 deals with structural geology. Faults occur, but as with the intrusives no connection with the origin of the carnotite deposits can be detected. Along Gypsum Valley a fault has a displacement of 2,000 feet.

Paradox Valley, the center of the carnotite region, is believed to be an eroded anticline, an idea to which not all geologists will agree, for others who have studied the region believe it to be formed by the sinking of a block. All the major folds involve the Mesa Verde (Cretaceous) sandstone and shale. The major folds are not strictly parallel but strike about northwest. They are shown by a special map (Plate II.).

In Chapter 4 carnotite and related minerals are discussed. The first shipment of ore, 10 tons, made by Gordon Kimball and others in 1898 from the Copper Prince claim on Roc Creek, carried 20 per cent. U_3O_8 and 15 per cent. V_2O_5. Few such rich shipments have since been made. The deposit happened to be in a tilted block of McElmo sandstone faulted down into contact with the Dolores and Cutler formations, giving the impression that the deposits were in the "red beds."

Concerning the occurrence of the carnotite deposits, Mr. Coffin says (pp. 153–157):

"The exploited carnotite deposits occur in the sandstones of the lower half of the McElmo formation as lenses, seams, and irregular pockets whose long dimensions follow in general the bedding of the sandstones. The larger ore bodies are associated with the massive beds generally near or at their base, but sometimes in the center or even at the top of these beds. Seams or lenses of greenish shale less than 2 feet thick underlie the ore and appear in places to have influenced its deposition. Shale, however, is not a constant factor in the occurrence of this ore, and in so far as it may have influenced the circulation of ground water its position is related to the present site of the ore deposits. . . .

"In many localities ore is not confined to one horizon and is often found at two or more levels within the same bed. At the Club Camp flat ore occurs in two massive sandstones about 40 feet apart; the upper one by far the more productive. At one place in the McIntyre District ore occurs at three levels; the distance from the upper to the lower occurrence is approximately 40 feet. At the head of Calamity Gulch ore was mined at several places from both the bottom and the top of a massive sandstone which was approximately 30 feet thick. All these occurrences were within the limits of the upper or important carnotite zone. . . .

"The upper limit of the important productive zone approximates the dividing line between the easily eroded shale portion of the formation above and the resistant sandstone portion below. This arrangement brings many ore bodies near or at the top of the bench which results from the uneven weathering of this formation. Much ore has been found on this bench so near the surface that it has been mined from open pits. . . .

"No carnotite was found by the present survey more than 400 feet stratigraphically above the base of the McElmo formation."

The ore bodies are usually 4 or 5 times as long as wide. The largest mentioned was at the Club Camp of the Standard Chemical Co., and was 450 feet long, 60 feet wide, and 1 to 4 feet thick. This body produced 2,000 tons of ore. The tenor is not given but it was probably 1.15 to 1.25 per cent. U_3O_8 and 4 to 5 per cent. V_2O_5.

The present position of the ore deposits is largely determined by the bedding and deposits are most regular in the most regularly bedded sandstones. In places the ore bodies descend from the usual level and follow the [cross] bedding, and in some places split.

Probably the most interesting form of the carnotite deposits is the "tree" or "log." It is not clear whether Mr. Coffin believes all of them to be replaced logs, but he apparently has doubts, as he refers to them as "cylindrical deposits or so-called 'trees' or 'logs,'" ranging from a few inches to 4 feet in diameter and 10 to 30 feet long, and again "Many of the so-called 'trees' and 'logs' are probably not related to any process of wood replacement."

I traversed the same region having as one of my principal objects the study of these peculiar deposits, having also studied them in the Utah carnotite deposits, and am convinced that they are replacements of real logs. They may be found in all stages from well petrified (silicified) round logs to flat ellipsoidal masses showing little resemblance to trees.

Unfortunately Mr. Coffin was unable to have made the analyses or the optical examinations warranted by the peculiar and complex mineralogy of the deposits, and the subject is lightly touched. He brings out the fact that the present minerals have migrated in recent time, but gives little consideration to their origin. He says that the origin cannot now be satisfactorily settled. He comes to a tentative conclusion concerning

deposits under deeper cover which I believe to be mainly correct, that the

"more plausible assumption is that ore bodies occur in deeply buried portions of the McElmo sandstone similar in form to the ones already exploited, but possibly differing in their mineral content."

The exception to be taken to this statement is that if bodies of unoxidized minerals should be found the ore bodies will be more concentrated.

As to the time of deposition of the ore bodies, Mr. Coffin can only say (p. 178) that he finds it hard to determine but suggests that they may have been deposited soon after the McElmo beds, though there has ceratinly been some recent movement of minerals. He reviews without decision the ideas advanced by various authors on the origin. He brings out the important fact that the ore bodies are found where the sandstones are massive, and states, what needs rigid proof, that the best deposits are located below conglomerates in which solid grains of minerals might have been deposited, dissolved, and precipitated below in the sandstone by organic matter. It is worth noting that so far pitchblende has never been recorded as having been found in placer deposits. It is too easily attacked by acids even to be found in the outcrops of deposits, let alone in clastic material moved around, ground up, and exposed to both mineral and organic acids, as were the contents of these beds. Only the complex compounds of uranium with tantalum, columbium, and the rare earths are known to stand the wear of stream gravels. No tantalum, columbium, or rare-earth minerals have been found in the region, so that the more complicated uranium minerals could not have been the source of the present oxidized minerals. Even were they found, they would not account for the vanadium minerals, for they have never been found in the pegmatite dikes in which the complex uranium minerals originate.

An error has been made in referring to the time required for equilibrium between radium and uranium (p. 185, foot note, and p. 186), as 500,000,000 to 800,000,000 years—50 to 80 times the actual period.

Methods of prospecting by drills of various types are described; costs and prices of ore are considered, and he estimates that 9,000 tons of ore carrying 2 per cent. U_3O_8 can be mined annually for a period of 5 to 15 years.

In Chapter 5 various important districts are described in some detail, and in Chapter 6 the small copper deposits near La Sal Creek; coal in the Dakota sandstone in First and Second Parks, west of Nucla; uncertain oil possibilities; and small manganese deposits and gold placers are described.

A short bibliography follows, and the work closes with an incomplete index.

FRANK L. HESS.

SOCIETY OF ECONOMIC GEOLOGISTS

This department has been established for the official communications of the Society of Economic Geologists whereby the affairs of the Society such as notices, minutes, titles of papers, elections, etc., may be brought regularly to the attention of its members.

Messrs. R. A. F. Penrose, Jr., and H. V. Winchell acted as delegates to the International Geological Congress held at Brussels early in August. Mr. George Otis Smith was unfortunately unable to leave the United States on account of the coal strike.

The Directors of the American Institute of Mining and Metallurgical Engineers have extended an invitation to the membership of the Society of Economic Geologists to attend the fall meeting of the Institute to be held at San Francisco, California, from September 25th to 29th inclusive. The two societies wil hold a joint session at which papers on ECONOMIC GEOLOGY will be presented and discussed. The members are earnestly requested to make every effort to attend.

Due to the absence of H. Foster Bain in Alaska, the Council on May 26, 1922, changed the Nominating Committee for officers for 1923 as follows:

ALAN M. BATEMAN, *Chairman*,
E. DEGOLYER,
GEORGE OTIS SMITH.

SCIENTIFIC NOTES AND NEWS[1]

H. Foster Bain, who has been inspecting the Alaskan coal fields, has returned to Washington.

E. K. Soper, manager of the Trinidad Tarouba Oil Development Co., has returned to New York from Trinidad.

W. C. Mendenhall has been making an inspection trip including visits to the United States Geological Survey parties engaged in field work in Montana, Wyoming and Utah.

W. Armstrong Price is now with the Humphreys Petroleum Company, at Dallas, Texas. He was formerly with the Transcontinental Oil Company of Mexico.

C. M. Bauer, W. B. Emery and L. P. Andresen are mapping the Kelvin area in Montana where a new oil field has recently been opened.

Julius Segall is at present geologist for the El Oro Mining Co., with headquarters at Mexico City.

Dean Winchester has returned to the United States, and has opened an office as Consulting Geologist, specializing in petroleum and oil shale. His address is 607 E. & C. Bldg., Denver, Colorado.

C. W. Washburne has changed his office to 2 Rector Street, New York.

W. T. Thom, Jr., has been transferred temporarily to coal statistical work from the oil and gas section of the U. S. Geological Survey.

T. A. Link, geologist of the Imperial Oil Co., is looking over possible drilling sites in the vicinity of Hay River, south of where it empties into Great Slave Lake.

Willet G. Miller has recently been in South Africa, where South African Geologists who visited Canada in 1913 were glad to renew their acquaintance with him.

[1] Geologists, mining engineers and others interested in applied geology are invited to keep the editor informed of new investigations of mining districts or scientific studies undertaken by them, together with such other scientific and personal items as may come to their notice

W. T. Lee, of the U. S. Geological Survey, has been detailed temporarily to the land-classification board to assist in coal-land classification.

William F. Prouty of the Department of Geology, University of North Carolina, has accepted a part time engagement as paleontologist for the West Virginia Geological Survey, and will spend his summer vacations in the field.

Lewis G. Westgate, with C. H. Dane and D. O. Hewett, has arrived in the Pioche district, in Nevada, for the U. S. Geological Survey.

L. R. Clapp will succeed J. A. Bancroft as assistant manager of the Granby Consolidated Mining, Smelting & Power Co.

E. A. Holbrook, the assistant director of the U. S. Bureau of Mines, has accepted an appointment as dean of the School of Mines of Pennsylvania State College.

B. D. Stewart now has charge of the Bureau of Mines' activities in Alaska.

W. Scott Turner has been visiting the Flin Flon copper property in Northern Manitoba.

Kirk Bryan, of the U. S. Geological Survey, is investigating public water supplies in New Mexico and Nevada.

C. R. Longwell, W. W. Rubey, and Alexander Stepanoff, of the U. S. Geological Survey, have gone from Newcastle to Upton, Wyoming.

David White was in Brussels as a delegate to represent the Government at the International Geological Congress.

M. R. Campbell, of the U. S. Geological Survey, has returned from his field trip and is at present assisting the Director as Acting Administrative Geologist.

Fred B. Ely has gone to Europe for an indefinite period to engage in the examination of oil lands.

Vernon F. Marsters' office address is now 920 Grande Avenue, Hayes Bldg., 5th Floor, Kansas City, Mo.

E. C. Andrews is Permanent Secretary of the Australian Society for the Advancement of Science, and is also the Australian representative of the Pan-Pacific Conference.

The Australian Association meets in New Zealand next January.

The next meeting of the Pan-Pacific Congress is to be held in Australia, the Australian Government having voted $24,000 for the purpose.

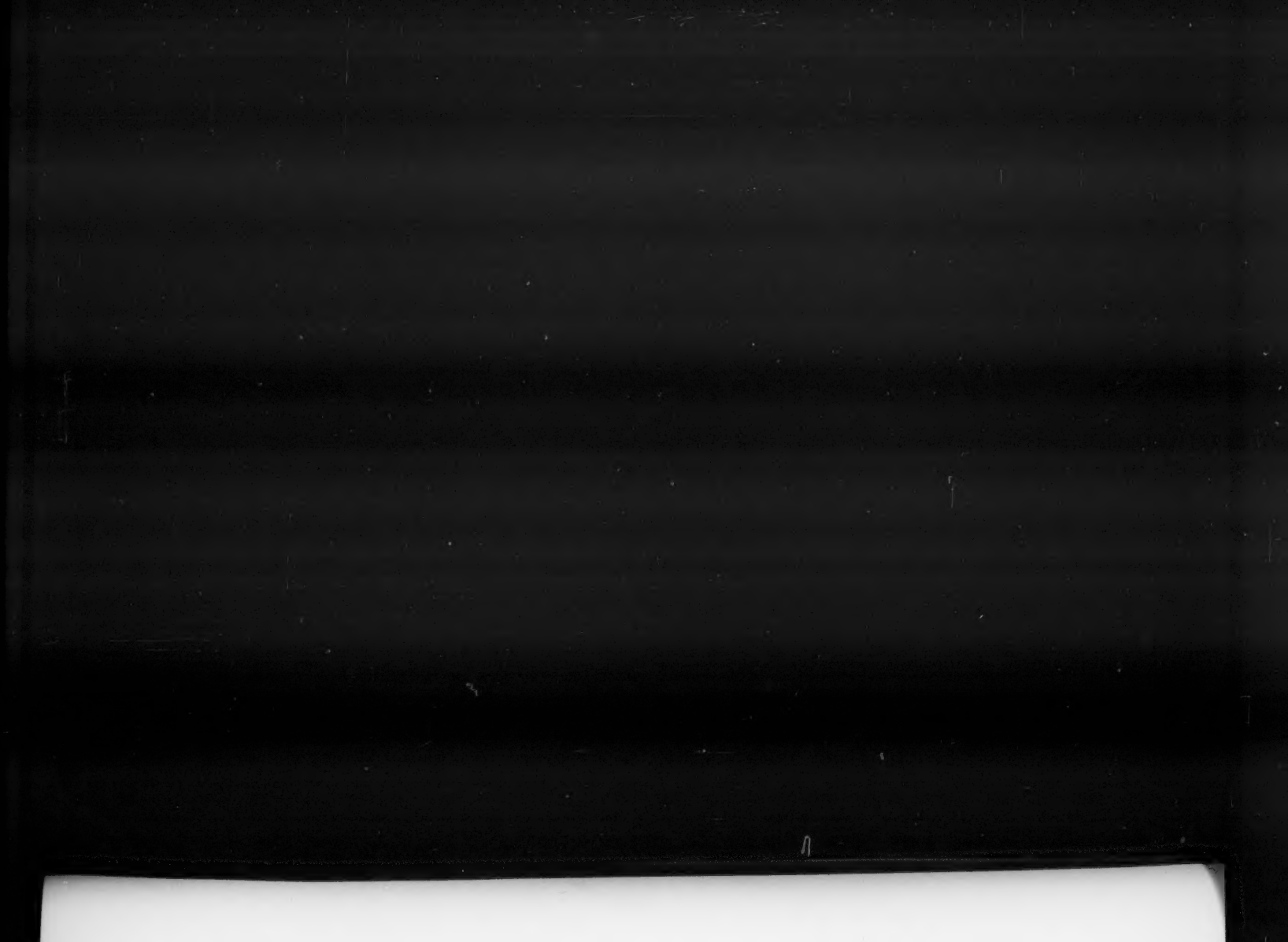
G. H. Cox, formerly of the University of Missouri and recently Chief Geologist of the Josey Oil Company, with headquarters in Oklahoma City, was instantly killed in an automobile accident near Bristow, Oklahoma, on August 19th.

L. G. Huntley and Stirling Huntley, formerly with Johnson, Huntley and Somers, have announced their association under the firm name of Huntley and Huntley, specializing in petroleum engineering and geology, with headquarters in the Frick Building, Pittsburgh, Pennsylvania.

Walter J. Yeaton, of the University of Illinois, was engaged during the summer by the Bureau of Economic Geology, University of Texas, to work on the Petrography of some of the sedimentary rocks of the state.

R. A. Daly and G. Palache, of the Shaler Memorial Expedition, together with F. E. Wright, of the Carnegie Institution, and Prof. Molengraaff, of Delft, have now left South Africa. During their stay they visited districts of igneous intrusions, such as the Bushveld Igneous Complex. South African geologists have enjoyed and benefited from their visits and discussions of geological problems, and also the friendly criticism of their work by sympathetic co-workers. Prof. Molengraaff and Dr. Wright gave interesting addresses on the subjects connected with the objects of the expedition, and at a dinner given by the Geological Society of South Africa on the departure of the visitors, Professors Molengraaff and Daly and Dr. Wright gave interesting resumés of the experiences of the expedition, and at the same time made highly appreciative references to the assistance they had received from local geologists and especially from the Geological Survey. The fuller results of their work will be awaited with considerable interest by geologists in general, and especially by those in South Africa, and will, no doubt, add considerably to our knowledge of large scale igneous intrusions, of which, in the opinion of the members of the expedition, South Africa possesses some of the finest and most clearly exposed examples.

The American Institute of Mining and Metallurgical Engineers holds its Fall Meeting at San Francisco, September 25–29. The following papers of interest to Economic Geologists are scheduled to be presented: British Columbia Batholith and Related Ore Deposits, and Deposition of Copper Carbonate from Mine Water, by P. D. Wilson; Ore Deposits

of Sierra Mojada, Coahuila, Mexico, by S. F. Shaw; Sampling and Estimating Orebodies in Warren District, Ariz., by R. H. Dickson; Sampling and Estimating Disseminated Orebodies in Sacramento Hill; Sampling and Ore Estimating at the Copper Queen Mines, Bisbee, Ariz., by R. W. Prouty and R. T. Green; Industrial Relations in California Petroleum Industry, by Roy W. Kelley.

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